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EXTRACT FROM OPERATING MANUAL (OM-34)
MASS SPECTROMETER AND LINE RECORDER VOLUME XIX

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Environmental Management Division
OAK RIDGE K-25 SITE
for the Health Studies Agreement

October 2, 1995

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OPERATING MANUAL

MASS SPECTROMETER
AND
LINE RECORDER

VOLUME XIX

This document consists of ___ pages.
No. 36 of 3? copies, Series A and
67 figures I. 1 through II. 30.

OPERATING MANUAL

MASS SPECTROMETER

AND

LINE RECORDER

VOLUME XIX

A-3349

FIRST EDITION

March 10, 1945

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II. LINE RECORDER

1. Description of Apparatus

a. The Mass Spectrometer Tube

In Section I of this manual, no mention was made of exactly how the various elements of an ion producing, mass analyzing system were assembled to give a practical unit, the mass spectrometer tube itself. Figure II.1-1 shows the design of the tube adopted for the present instrument.

The source end is housed in a glass envelope which is attached to the copper analyzer tube by means of a Kovar-to-glass seal. The tubing surrounding the collector plate is made of nickel rather than copper to avoid the evaporation of metal on the insulation supporting the collector lead.

The gas to be analyzed is fed into the instrument through the gas inlet as shown and is pumped away through the 1-5/8" copper pump lead shown. By feeding the gas directly into the source, the pressure there will be considerably higher than in the rest of the apparatus, a feature which is desirable since it gives the maximum possible ratio of incoming to residual gas pressure.

In the sectional drawing "AA" the filament F is heated to give an electron beam which is caught by plate T. This electron beam is kept accurately aligned by means of a magnetic field produced by an Alnico magnet which surrounds the tube; the magnetic field may be in either direction. The two poles of this magnet are indicated in the drawing. Referring to the main drawing, we see that the electron beam cross section is indicated as a heavy dot immediately above the slit in plate S, the shield.

Ions formed by collision of the electrons with the gas molecules are drawn through the slit in S and accelerated through a series of plates J1, J2, J3, J5 and G. J1 and J2 are a split pair and permit one to bend the beam to one side or the other to compensate for imperfections in the alignment as well as for the slight bending of the ion beam produced by the magnet field used for aligning the electron beam. The remainder of the plates form a lens which not only increases the intensity of the ion beam entering the magnetic analyzer, but also prevents a dropping off of ion intensity for all but the lowest energy ions. The two plates marked G are grounded along with the magnetic analyzer housing to which they are tied. Two plates are used instead of one for mechanical reasons only. The following table gives tentative operating currents and voltages for the ion source.

Total Electron Emission	100 to 200 x 10^{-6} Amps
Electron Trap Current	At least 90% of total electron emission
Electron Accelerating Potential.	75 $\pm$ 5 Volts
Potential between S and J1	100 Volts
Potential between S and J2	Almost identical to J1
Potential between S and J3	120 Volts
Potential between S and G	Adjustable 0-2500 Volts
Potential vetween J5 and G	0.6 of potential SG

Since the ions are formed in the box attached to S, it is obvious that the potential drop SG is equal to their energy when they enter the magnetic analyzer. The radius of curvature of the center line of the analyzer tube is 7.62 cm. Mass 14(N+), the lightest ion we intend to measure, should be collected when its energy is 2100 volts, slightly less than the maximum available voltage. Thus, according to Equation (11) of Section I.5, the field strength of the magnetic analyzer should be given by:

$$14 = 4.82 \times 10^{-5} (7.62)^2 H^2 / 2100$$

or

$$H = 3250 \text{ gauss}$$

Also, according to this equation, the mass of the ion collected is inversely proportional to the voltage applied between S and G. Thus, mass 28 (CO+ or N2+) will be collected when the potential from S to G is 1050 volts, etc.

Energetic ions striking a surface will release secondary electrons of low energy. In order to prevent any such secondary electrons emitted at or near the collector from being collected and hence giving false readings on the amplifier, a weak magnetic field (not shown in drawing) produced by a small permanent magnet is directed across the tube and parallel to the slit in front of the collector.

b. Vacuum and Gas Connections to Spectrometer Tube

Figure II.1-2 shows the vacuum and gas connections employed on the line recorder frame. These connections have the function of admitting the gas sample to the spectrometer tube and providing means for continuously evacuating it. Means are also provided for introducing a small quantity of argon into the gas stream as a calibrating gas to show any changes in sensitivity caused by the aging of the tube, etc. (It is recommended that this argon equipment be removed;cf Section II.2-b). A metered sample of gas is introduced at the tube rack gas inlet and flows through the chemical trap 151 into the spectrometer tube. This gas sample may contain 616, 816, nitrogen, oxygen, and possibly certain other gases. The chemical trap removes the 616 but leaves the other components unaffected. The flow of 616 present is determined from the total flow rate by subtracting the flow of impurities. The impurities are

determined from the readings of the spectrometer. In order to evacuate the spectrometer tube, diffusion pump 159 is employed. Ion gage 160 is used to measure the pressure at the pump lead while the diffusion pump serves to maintain the high degree of vacuum required for the successful operation of the spectrometer tube, namely 10^{-5} to 10^{-7} millimeters of mercury. The diffusion pump is "backed" by the fore pump. The oil trap is included so that, in the event that the fore pump should fail, the oil from the fore pump will not be drawn into the diffusion pump. Fore pumps are guaranteed against this oil leakage, but even the best pumps sometimes "back up" if left over night with a vacuum above them when they are not running. In order that this should not occur during normal shut-down, valve 164 is provided by which the system may be vented to the atmosphere. Thermocouple gauges 162 and 165 are provided for measuring the fore vacuum, 162 at the diffusion pump and 165 at the fore pump. Two gauges are provided so that the diffusion pump may be isolated and the fore pump used for other pumping at times. Valve 163 is provided for this purpose. This is permissible because the design of the diffusion pump used on the line recorder is such that the diffusion pump can operate for a period of about fifteen minutes with typical operating flow conditions without the fore pump, before the fore pressure rises to the point where the diffusion pump ceases to work. Valve 153 is incorporated so that the diffusion **fore** pump may be used to pump down the gas lead before opening it to the spectrometer, after making any changes.

The dotted lines indicate the system for admitting argon. The leak 167 is a very small pinched tube and is such as to drop the pressure from atmospheric to about 10^{-7} mm of mercury and hence provides a very small flow. Reservoir 156 is for storing argon and is kept at a pressure of 5 psig. Valves 161 and 158 are used for refilling the reservoir with argon and are equipped with a fitting to which an argon tank may be attached. A fore pump connection through valve 157 is included to evacuate the reservoir before filling.

c. <u>Electrical Connections between Components of Line Recorder</u>

In order that the line recorder may function, it is necessary that certain voltages and currents be supplied to the spectrometer tube and that some means be provided to measure the ion current and gas flow. It is also desirable that the pressure at the tube be measured. For these reasons and to record the results of the analysis, certain electronic components are required. A schematic diagram of these electronic circuits and their electrical connections is included as Figure II.1-3. The voltages which are required for the operation of the spectrometer tube are provided by the high voltage supply, control panel, and emission regulator.

The function of the high voltage supply is to furnish 2500 volts D. C., the negative side of which is grounded; the supply is operated with 115 volts A.C. supplied from the control panel.

The function of the control panel is to divide up the high voltage so that the proper accelerating voltage appears at the source. The potential of J5 is also provided by the control panel.

The emission regulator furnishes voltages for the remainder of the source and provides filament current so regulated that the total emission remains constant.

The ionization gage (ion gage control and ion gage tube) serves to indicate the pressure at the spectrometer tube and is equipped so that it will turn itself and the spectrometer tube filament off in case the vacuum should become bad, so poor that there is a possibility of burning out a filament. The electronic part of the ion gage performs a triple function. It provides the ion gage with operating potentials, furnishes it with filament current regulated so as to hold the emission constant, and measures the ion current of the ion gage tube.

The preamplifier and amplifier serve the important function of measuring the ion current. These currents may be as small as 10^{-12} amperes and still be measurable. The amplifier consists essentially of a sensitive vacuum tube voltmeter having a 5×10^9 ohm grid resistor. The unit includes a power supply furnishing well regulated direct current for the operation of the amplifier and preamplifier.

The voltage stabilizer is a commercial stabilizing unit which is intended to smooth out the fluctuations in the 115 volt alternating current obtained from the mains. This makes the design of the regulated power supplies in the other units much simpler since they do not then have to cope with such large fluctuations.

The Pirani gage control serves the function of providing a means of reading the flow and provides the necessary voltage to run the gage. The Pirani gage is used to measure the flow rate so that any variations in it affect the accuracy of results; hence, the care exercised in this seemingly simple unit.

The last but by no mean least important unit is the recorder. This unit is the "brain" of the line recorder and serves the purpose of recording the sizes of the ion peaks corresponding

to the various gas components to be measured and the Pirani gage reading. To do this, the recorder switches the voltages on the spectrometer tube to the required value for each ion to be measured, selects the sensitivity of the amplifier, and records the output of the amplifier. The ion peaks are thus examined in some prearranged sequence which is continuously repeated. The result is a set of curves which show the variation of each component with time.

The cable connections between these various units are indicated in Figure II.1-3 and any numbers referred to will be from that figure. Cables 1-3 and 2-4 connect the ion gage circuit with the ion gage tube, one carrying filament current and operating voltages and the other carrying the plate current of the tube to the control circuit for measurement. Cable 5-10-36-17-28-30 is a stabilized 110 volt feeder carrying current to the various units. Cable 6-8 carries alternating current to the emission regulator to operate the filament, which will be turned off if the pressure rises above the safe limit. Cable 7-11 carries operating currents and voltages from emission regulator to tube source while cable 9-15 carries the accelarating voltages from control panel to emission regulator. Cable 16-23 carries high voltage from the high voltage supply to the control panel and cable 19-25 supplies the high voltage supply with power. Cable 18-33 enables the recorder to control the accelerating voltage while cable 27-34 enables it to select the amplifier sensitivity and carries the amplifier output to the recorder for measurement. Cable 12-13 connects the Pirani gage with its control while 14-32 feeds the Pirani gage signal to the recorder. Connection 20-21 carries the ion current to the preamplifier for measurement and cable 22-26 interconnects preamplifier and amplifier. Cable 35 connects the recorder with one or more master recorders. Connections 25 and 29 are to ground. Connection 31 brings in the operating voltage supply.

d. Electronic Units

The subject matter of the following is the description of the various units contained in the relay rack.

The appearance of the front panel of an ionization gage is indicated in Figure II.1-4. The controls are labelled and have the following functions:

The instrument (in this section all titles on the panels are underlined) switch is a meter switch by means of which the one meter may be used for several purposes. In the position labelled check emission, it reads the amount of filament emission and should

read 8 on the scale. The second position, <u>check sensitivity</u>, is used to measure the sensitivity of the amplifier portion of the ion gage control. The meter should read 5 at this position if the amplifier is properly balanced according to the methods that follow. In the third position, <u>ion gage</u>, the meter reads pressure in the line recorder tube. The fourth position, <u>ion gage automatic</u>, is the same as the third except that the ion gage will turn off both filaments in the vacuum system if the pressure becomes high enough so as to endanger the filaments. The <u>scale factor</u> switch determines the factor by which the meter reading is multiplied to give the tube pressure in millimeters of mercury absolute. The <u>scale factor</u> switch should be left in the off position when making other tests. The ion gage amplifier may be balanced by setting the <u>scale factor</u> switch to the <u>off</u> position and the <u>instrument</u> switch to one of the ion gage positions. The knob labelled <u>balance</u> is then adjusted until the meter reads zero.

If the meter does not read 5 on the <u>check sensitivity</u> position of the <u>instrument</u> switch after the amplifier has been balanced as described above, the screwdriver adjustment labelled <u>adjust</u> located under the label <u>sensitivity</u> should be set so as to obtain this reading.

If the <u>emission</u> does not have its proper meter reading of 8, the knob labelled <u>regulate</u> should be adjusted until a point is found at which a small change of that knob produces very little or no change in the emission. If the emission still does not give a reading of 8, the screwdriver adjustment labelled <u>adjust</u> located under the label <u>emission</u> should be set to give the proper value of emission. The <u>regulate</u> knob should then be checked again to see that the knob is so set as to have a very small effect on the emission. If such is not the case, the process just described should be repeated.

The switch labelled <u>power</u> is a warm-up switch and is turned on several minutes before the other switches. The push button labelled <u>filament on</u> is pushed to turn on the ion gage itself. This should not be done unless a sparker applied to the glass of the vacuum system indicates a good vacuum. If no glow or only a very pale one is seen when the glass near the diffusion pump cold trap of the tube rack is touched with the sparker and if a pronounced greenish blue glow is seen from the mercury jet in the mercury diffusion pump when the sparker is applied to the upper portion of that pump, the pressure is low enough that the ion gage may be safely tried. It is of no use, however, to try the ion gage unless the cold trap of the diffusion pump has been cooled with liquid nitrogen or dry ice slush, since the vapor pressure of mercury is above the upper pressure limit of the ion gage at room temperature.

The trip push button is included to check the cutoff feature and when pushed, should turn off the ion gage. The grid switch allows the grid of the ion gage to be heated vigorously when turned on and may be of some use in obtaining a somewhat higher degree of vacuum on a new or recently opened system. The grid should not be heated unless the "black vacuum" test has been passed. When heated thus, the reading of the ion gage will increase considerably but, after a few minutes, will generally begin to drop back toward normal. The grid should not be heated for more than an hour or two at a time since further heating does little or no good. During normal operation this feature is not used.

If the pressure is sufficiently low, the ion gage may be turned on. This is done by turning the power switch to the on position and waiting for a few minutes, after which the filament on button may be pressed. This should be done with the instrument switch in the ion gage automatic position. When this is done, the filament on the ion gage should light and a red light should appear on the front panel above the push button. If the pressure is higher than the value at which the ion gage turns itself off, the pilot light will light momentarily and go out. The value at which this happens should be about 5×10^{-5}, which can be determined roughly by setting the scale factor switch to the 10^{-5} position and observing the meter when the filament on button is again pressed. If the meter reads zero before the button is pressed and goes up to three or higher after the button is pressed, and then the filament turns off, the pressure is actually higher than the accepted value and one should wait for five or ten minutes and try again. If one suspects that the pressure is only slightly higher than the "cut off point", the pressure may be measured by turning the scale factor switch to 10^{-4}, the instrument switch to ion gage, and pressing the button. If the pressure is below 2×10^{-4}, the ion gage may be left on for short periods of time, but the emission regulator should not be turned on. During normal operation of the ion gage, the instrument switch should be in the ion gage automatic position and the scale factor switch should be turned as far in the clockwise direction as it can be without getting the meter off scale. The sensitivity, trip, and balance should be checked occasionally as described before.

The appearance of the front panel of an emission regulator is shown on Figure II.1-5. The emission regulator, as its name implies, controls or regulates the electron emission from the heated tungsten filament located in the line recorder tube source. Its electronic circuit is designed so that constant emission is obtained even though the filament current requirements should change, as is the case when the line recorder tube pressure is changed. It also compensates automatically for any change in the voltage of its source of power. In addition to regulating emission, the emission regulator provides a stabilized

voltage supply for use in accelerating the electrons and maintaining the proper potentials on the trap, J1, J2, and J3. The procedure for operating this unit properly is in many ways similar to that for the ion gage. Once the pressure in the line recorder tube has become 5×10^{-5} millimeters of mercury or less, the emission regulator may be turned on. The proper procedure in doing this is as follows:

1. Throw power switch to on position and allow a minute or two for warm up.

2. Set instrument switch to emission x 4 and set coarse emission switch to position 7. Also turn regulate knob counterclockwise as far as possible.

3. Throw filament switch to on position and turn regulate knob slowly clockwise while watching the 0 to 50 microampere meter. As the regulate knob is turned the emission will be observed to rise to a definite value and then show little or no change in emission as the regulate knob is turned clockwise through a considerable angle. If the regulate knob is turned clockwise a sufficiently large amount, the emission will again rise. However, the proper adjustment of the regulate knob is in the region where slight changes in its position does not result in a changed emission.

4. The actual amount of emission required is now obtained by adjusting the emission control knobs. If a large adjustment is required the regulate knob should be readjusted to insure that it is in the operating range. Generally the emission should be between 100 and 200 microamperes. Should emissions less than 50 microamperes be desired, the instrument switch provides a tap, X1, which decreases the range of the emission meter by four.

To measure the trap current, the instrument switch is thrown to the trap position. When the source magnet is properly adjusted, the trap current will be at least 90 per cent of the emission current. An A. C. ammeter (shown on the left side of drawing in Figure II.1-5) is provided to measure the current required to heat the filament. The reading over a long period of normal operation will be observed to decrease slowly due to deterioration of the filament. Its principal purpose is to give some indication of the filament conditions.

An emission regulator properly functioning may be recognized by observing that there are no changes or fluctuations in emission current even though the line recorder tube pressure changes. Also, the change in emission with position of the regulate knob will be practically zero for reasonably large changes in the regulate knob position.

The setting of the focus control knobs is immaterial insofar as the regulation of emission is concerned. The coarse adjustment knob of J1 and J2 is generally set on position 6. Position 7 is generally the value for J3. J4 is at present not used. J1 is adjusted in the process of tuning up the tube.

The Leeds and Northrup sixteen point automatic self balancing recording potentiometer (shown as "Recorder" in Figure II.1-3) serves as the "brains" of the line recorder. It has two principal functions:

1. It selects the proper high voltage to measure a given peak and simultaneously selects the proper sensitivity shunt to keep the peak being measured at the proper place on the recorder chart. In effect, the recorder sets the program which governs the peaks to be scanned by the line recorder. The line recorder is so constructed that it can scan eight different masses (corresponding to the eight channels, A to H), the Pirani reading, and the amplifier zero. The L & N recorder determines in what sequence, and with what frequency, these are printed.

   In a typical sequence of sixteen points, the recorder might print mass twenty-eight eight times (every alternate point), mass sixty-nine twice, the Pirani twice, and each of masses twenty, thirty, forty-four, and the amplifier zero once.

2. The L & N recorder records, by printing upon a chart, the intensities of the various peaks the line recorder scans at the time the peaks are scanned. The motion of the chart provides the time scale.

The L & N recorder is driven by a synchronous motor (not shown in any drawings) which supplies both the motive power for the device and the time scale for all its functions. The chart consists of a roll of specially printed paper with a working width of ten inches. There are a hundred and one equally spaced lines running vertically along the roll, at one-tenth inch intervals, with fifth and tenth lines accented. The chart moves down at a fixed speed which, in the line recorder, is usually three inches per hour. Horizontal

Lines are printed at half inch intervals, so that there is a horizontal line for every ten minutes of record. A sample of chart, as printed, is included in Figure II.1-6. The points to be recorded are printed by a print wheel which prints in sequence a, 1, b, 2, c, 3, d, 4, e, 5, f, 6, g, 7, h, and 8. (On all except the first few units, the print wheels will have various symbols, such as dots and crosses, rather than the letters and numbers.) Each of these points is inked by a separate ink pad, so that color coding may be used in addition to the letters as printed.

The print wheel is shifted from one point to the next in sequence by a cam arrangement once every twenty-four seconds. Simultaneously, two commutators built into the recorder are also shifted. One of these commutators supplies the operating current for the relays in the control panel which select the point on the high voltage divider from which the accelerating voltage is picked and in this manner determine the peak to be measured. When printing amplifier zero, the commutator actuates a relay which alters the voltage on plate J3. The accelerating voltage is zero. When printing the Pirani, the Pirani circuit is connected directly to the L & N recorder in place of the output of the amplifier.

The second commutator carries the amplifier output, selecting which of the sensitivity switches on the amplifier panel shall be used to control the sensitivity of the signal being recorded. For both amplifier zero and Pirani, the signal is automatically recorded at maximum sensitivity.

While any given sequence of operation could be determined by the internal wiring of the L & N recorder, much greater flexibility is obtained by wiring the program connections in an AN connector (with twenty-six contacts) which is screwed into the back of the recorder. Two such "program plugs" are required for each recorder, one for the sensitivities, and the other for selecting the accelerating voltage. Then, in order to change the program, one merely unscrews the program plugs for the old program and inserts plugs wired up to give the new program.

The amplifier panel layout is pictured on Figure II.1-7. The amplifier is a hundred per cent negative feed back amplifier, so that no voltage amplification occurs. However, extremely high current amplification takes place, so that ion currents on 10^{-12} amperes and greater are brought up to convenient values. (About a half milliampere.)

As is characteristic of direct coupled amplifiers, the zero reading (reading for zero input signal) will shift slightly with time. This drift is rather great when the amplifier is just turned on, but after several hours has decreased to reasonable values and after some twenty-four hours of operation will be, when the amplifier is operating properly, one or two scale divisions on the recorder, on the most sensitive shunt, in

The amplifier output may be read on the output meter mounted on its panel. This output meter has a sensivivity shunt of its own, which is controlled by the sensitivity switch immediately beneath it. When on shunt x1, the output meter reads twenty millivolts full scale. Since the meter is divided into ten divisions of two millivolt units each, each division on the output meter corresponds to a scale division on the L & N recorder, when the recorder is operating at its maximum sensitivity. For other sensitivities than x1, the reading of the output meter (or, of course, the recorder) is multiplied by the number at the sensitivity switch.

Coarse, medium, and fine zero adjustments (marked balance) are included on the panel. To adjust the zero, the accelerator voltage selector of the main control panel (Figure II.1-8) is set to off position and the balance switches so adjusted that the output meter reads zero on the most sensitive shunt.

In addition to the sensitivity switch for the output meter, there are eight sensitivity adjusting switches marked A to H mounted on the amplifier panel for each of the eight channels provided by the main control panel. The zero is always printed at maximum sensitivity, so that it requires no switch. The path of the amplifier output when actuating the L & N recorder is as follows: From the amplifier to the commutator, through the commutator to the program plug that selects sensitivities, thence to one of the eight sensitivity switches on the amplifier panel, thence back to the recorder galvanometer through the sensitivity voltage divider in the amplifier.

Due to the long period required by the amplifier to reach equilibrium, so that zero drift reaches its proper low value, it is advisable to keep the amplifier on at all times, even when a tube rack has no vacuum in it. The first two stages of amplification take place not in the amplifier circuit proper, but in a preamplifier which is mounted on the tube rack. This arrangement minimizes shielding and leakage problems for the very small ion currents being measured. The amplifier should not be turned on unless it is properly connected to the preamplifier, although it is not necessary that the preamplifier be connected to the spectrometer tube.

The main control panel is pictured in Figure II.1-8. Its primary function is to set and control the switching of the accelerating voltage applied to the mass spectrometer tube. Some twenty-five hundred volts are brought from the high voltage supply to the main control panel. Here, this voltage is applied, through a variable resistance called the trimmer, to two voltage dividers. One of these, the manual divider, is adjusted by three switches on the front of the panel; the accelerating voltage can, by use of this divider, be adjusted to any voltage from the maximum (as supplied by the high voltage supply minus the drop in the trimmer) to zero.

The other divider is made up of a series of potentiometers and fixed resistances. The center taps on the potentiometers are adjustable with screwdriver adjustments on the front of the panel, to give a variety of fixed accelerating voltages. Eight of these fixed points are connected to relays (labelled A to H) which, when closed, connect their corresponding point to the tube. The manual divider is also connected to a relay which serves the same function. A tenth relay is used to change the voltage on J3 when the amplifier zero is desired.

The operation of the relays is controlled by the switch marked acceleration voltage selector. This switch, when turned to the record position, supplies the voltage selector commutator in the L & N recorder with a voltage source which is used to actuate (through the program plug) the relays in the control panel. All but the manual relay may be actuated in this manner. If it is desired to have the L & N recorder select the voltage at which the manual divider is set at one or more print points, it is necessary to connect one of the eight relays (corresponding to one of the eight channels available) to the manual divider.

When the acceleration voltage selector is turned to the point check position, the relay actuating voltage goes, not to the commutator, but to the point selector switch. This switch is connected, in turn, to each of the eight relays that give rise to the eight available channels. Hence, when the point selector switch is turned to position C, relay C is shut, thus applying to the spectrometer tube the accelerating voltage determined by the point on the fixed voltage divider to which relay C is connected. The eight screwdriver adjustments on the front panel corresponding to the eight relays are tagged with the appropriate letters. If the internal connections of the panel are changed, so that say relay B is connected to some other fixed point, the tag B on the front panel is moved accordingly.

When the acceleration voltage selector is turned to manual, the accelerating voltage determined by the manual divider is applied to the spectrometer tube due to the closing of the proper relay. When it is turned to either off position, the voltage on J3 is altered so that the amplifier zero can be determined.

The voltage on plate J5 is set by the focus switch on the main control panel. For this purpose an auxiliary voltage divider is installed across the voltage output to the spectrometer tube. This divider is used to make the voltage on J5 some fixed (but adjustable on the panel) fraction of the total accelerating voltage.

The trimmer is used to set the overall voltage across the fixed divider so that the range covered by each of the fixed points will be sufficiently great to enable setting of the voltage to properly adjust that peak in the tube. The trimmer enables one to take into account the slightly different magnetic field intensities that may be supplied by the main magent. It will usually be sufficient to adjust the trimmer if the high voltage changes slightly, rather than to adjust each individual fixed point separately.

e. Manifold Assembly

In the K-25 plant there are two line recorders for each building. For use in the plant, some means of bringing a sample of the gas to be analysed to the tube rack is essential, as are methods of calibrating the instruments. The manifold assembly, to which the tube racks are connected, contains the auxiliary equipment necessary to enable the efficient use of the line recorders in analyzing the process stream. The manifold assembly, a flow sheet of which is given in Figure II.1-9, contains the following equipment:

1. Leaks to control and Pirani gages to measure the gas flow to the tube racks.

2. A series of valves and headers to enable either line recorder to be connected to any cell in the building while the other line recorder is connected to any other (or the same) cell.

3. Calibrating samples for static calibration of the line recorder.

4. Pumping equipment to enable the determination of residuals, the static calibration, and the operation of the sampling manifold.

5. A sampling manifold to enable the removal of samples of the plant stream from any cell.

6. Air flow and process stream flow measuring apparatus for the dynamic calibration of the line recorders.

7. Connections to the dry nitrogen supply to enable purging of the sample lines in a cell to be shut down.

The manifold assembly is air conditioned in those regions in which the sample stream flows. A list of the various parts of the manifold assembly (Figure II.1-9) follows. Valves are not included in this list. A globe or angle valve is indicated —▷◁— and a tee valve
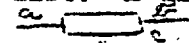
A tee valve always permits flow from a to b, and permits flow to c when the valve is opened.

PARTS LIST FOR THE MANIFOLD ASSEMBLY
(Figure II.1-9)

Parts listed do not include valves, except for 109

Part Number	Description
(1) through (14)	Incoming and outgoing sample lines from cells (1) through (14)
71 through 74	Adjustable leaks
105	Mixing Venturi

Part Number	Description
106	Venturi for measuring flow
109	Special needle valve for adjusting flow
110, 111	Rotameters for measuring air flow
112, 119	Thermocouple gages
113, 114	Pirani Gages
115, 116	Bottles to hold calibrating samples
118	Sample Tube
120	U trap for sampling manifold
120-1, 120-2, 120-3	Special Couplings
121	Fore pump
122	Oil trap
123	Mercury Diffusion pump
124	Cold Trap
125 through 128	Flow proportioning resistances
129	Air filter
145, 146	Copper sweat couplings

The tube rack is described in Section II.1-b of this manual. There, in Figure II.1-2 is shown where gas enters the tube rack. The pressure at the gas inlet under normal operating conditions is a few microns. It now remains to be shown how the flow of gas samples or unknowns into the tube rack may be controlled.

The necessity of controlling the gas flow into the tube rack arises from two factors:

1. The pressure in the sample line may vary from a centimeter or so to some 60 centimeters of mercury.

2. The tube rack is built to operate at Pirani gage reading near 50, (100 millivolts) which corresponds to a flow of 40 mg of 616 per day or 1/40 cc mm/sec.

These conditions are sufficiently rigorous that such a valve must be constructed in a manner quite different from an ordinary valve. The device constructed for the job is called an adjustable leak and is shown in Figure II.1-9 and II.1-10.

(The leak is adjusted by turning the handle of the clamp which in turn causes the shoes to move on the inclined planes, thus increasing or decreasing the pressure of the jaws on the leak tube. The compression of the tube about the snug-fitting plug controls the gas flow. The capillary at the entrance to the leak is used to prevent fractionation of the gas passing through the leak. If it were not present, the composition of the gas entering the tube rack would not be the same as that of the sample under analysis.) Evidence that the capillary tube actually prevents such fractionation is presented later in this report.

The Pirani gage consists of a Monel block drilled to receive
a nickel filament wound of three mil nickel wire. The gas flowing to
the tube rack is admitted to this opening. The nickel wire is heated
by a current from the Pirani gage circuit. The effective resistance
of the wire is then dependent upon the pressure in the opening. (See
further Section I.1). The Pirani circuit is a bridge circuit with the
Pirani filament as one arm of the bridge. Another arm of the bridge
consists partially of a nickel resistance mounted in the same block as
the Pirani filament so as to give temperature compensation. Tempera-
ture compensation can be obtained in this manner only at some definite
operating point of the Pirani. Two such circuits are built in one unit,
the front panel of which is pictured on Figure II.1-12.

The Pirani circuits obtain their power from the voltage stab-
ilizer. A transformer plus a rectifier in each circuit gives a pulsating
direct voltage supply of constant amplitude. This voltage is applied
across the bridge through a variable resistance which is adjustable from
the front of the panel to enable setting the total bridge current to its
correct value of 90 ma. This adjustment must be made carefully as a two
per cent change in bridge current will correspond to approximately a five
per cent change of output, in the opposite direction.

The output is read on a meter connected across the bridge in the
conventional manner. The reference point on one side of the meter is ad-
justable so that the bridge may be balanced at zero pressure. The meter
reading is then, over a limited range, nearly proportional to pressure.
The meter used reads 100 mv. (fifty recorder scale divisions) full scale
and may be adjusted to read 200 mv. full scale by throwing the meter
switch to the down position. The L & N recorder is connected to the
same points of the bridge as the output meter.

In order to facilitate the description of the operation of the
manifold assembly, its use in the various functions for which it is in-
tended will be discussed individually. Flow diagrams are included in
which the parts of the manifold assembly used in each specific function
are accented to show the manner of operation. When a change is made in
manifold operation, necessary valves are closed before any are opened.

Normal operation of the line recorder which will occur for
the greater portion of the time is shown in Figure II.1-13 for the case
where tube rack A is connected to cell (1) and tube rack B to cell (14).
The paths of the sample streams are indicated by the heavy lines. The
dotted lines indicate the sample of gas bled through the leaks to go
to the tube racks.

NORMAL OPERATION OF THE LINE RECORDER

The spaces between leak 73 and valve 83 and between leak 74
and valve 84 are shown evacuated, as is necessary to get a true analy-
sis, since any gas behind these leaks would go through them and mix
with the gas being analyzed. This space has, as a precaution, to be
evacuated at least once a day. It would seem the best procedure to
pump on it continually by leaving valves 83, 84, 91, 92 and 96 open
except when it is necessary to use the diffusion pump for some other
purpose.

Figure II.1-14 shows the setup for determining residuals on tube rack A while tube rack B is connected to cell (14). Before valves 99 and 98 are opened, liquid nitrogen should be placed on cold trap 124 to trap the 616. Note that valves 80 and 82 are opened to pump out the space up to valve 78 preparatory to using the sample in bottle 116.

After the residuals are determined, valve 91 is shut and valve 78 opened to admit the sample in bottle 116 to tube rack A. Figure II.1-15 shows the conditions in this case.

The final step of the static calibration is the calibration with air. To do this, the space behind leak 74 must be evacuated which is done by closing valve 78 and opening valves 91 and 92. This is shown in Figure II.1-14. When a vacuum has been attained, valves 96, 98 and 99 are closed and valve 100 opened admitting air behind the leak. Valve 100 should be opened partially and then closed again since the pressure behind the leak need not be atmospheric. This condition of operation is pictured on Figure II.1-16.

In order to return the machine to normal operation, valve 100 is closed and valves, 96, 59 and 67 are opened. The cold trap, 124 is also warmed up with the heater provided for that purpose. The liquid air is, of course, removed before warming up the trap. When the cold trap is warm, valves 99, 62 are opened to discharge the trap into the process stream after which valve 62 is closed. When a vacuum is attained behind leak 74, valve 84 may be closed. This returns the instrument to the condition shown in Figure II.1-13.

The line recorder may also be calibrated dynamically. This is done by measuring the flow of gas in the sampling lines and adding air at a known rate. This increases nitrogen and oxygen contents of the analyzed gas by a known amount and thus affords calibration information. The means by which this is done are shown in Figures II.1-17 and II.1-18. Provisions have been made for the addition of air only to the gas flowing into incoming header X so that the conditions for calibrating tube racks A and B are not identical.

The calibration of tube rack A is shown in Figure II.1-17. For this operation, the manifold is as it is used for normal operation except that valves 57, 61, 109, and either 101 or 102 are open. Valve 109 is a valve capable of fine adjustment that is used to control the flow of air into the manifold. The flow in the sample line is measured by means of the Venturi meter, 106, while the flow of air is measured by either of two rotameters. The low range rotameter is used whenever it is on scale in order to obtain as much accuracy as possible. If the desired flow of air can be obtained with either valve 57 or 61 closed the calibration should be made in that manner since the operation of the mixer is more efficient under these conditions. It will be noted from Figure II.1-17 that valves 60 and 70 are also open. These valves are opened to by-pass some of the gas from the sample lines in case there should be more flow than can be read on the Venturi meter. These valves are to be regulated to bring the flow to some suitable value. To return from dynamic calibration to normal operation, it is only necessary to close valves 57, 61, and 60 if they were open.

The dynamic calibration of relay rack B is shown in Figure
II.1-18. When the calibration is made thus, the gas from incoming
header X flows past tube rack B and into outgoing header Y. Gas from
incoming header Y flows past tube rack A and into outgoing header X.
This fact must be remembered when connecting these headers to the
proper sample lines. The operation of the air addition equipment
is the same as when calibrating the other tube rack. In the event
that it should prove necessary to use valves 60 and 70 to bypass
a part of the flow, valves 58, and 67 should be closed and outgoing
header X should be connected to the same sample line as outgoing
header Y.

The actual description of the manner in which the sample
manifold is manipulated to take a sample for analysis will not be
discussed here. The manner in which the sample may be brought to
that manifold will, however, be mentioned here. In one case it
is necessary to stop using at least one line recorder temporarily.
The manifold flow sheet for such a process is shown in Figure II.
1-19. The gas from cell 2 flows through incoming header Y past
the leak for tube rack B through the sampling setup and out through
outgoing header X. Valves 59 and 67 are closed as are all valves
on outgoing header Y.

TAKING SAMPLES

Another manner of removing a sample proceeds as follows:
The volume enclosed by valves 90-1, 68, and 69 is flushed out with
74. Valves 68 and 69 are then shut and this space is evacuated
through valve 90-1. When a sufficiently good vacuum is obtained,
the sample may be admitted through either valve 68 or 69 into bottle
120, after which valve 90-1 is shut. By use of this method, a sample
may be taken from either of the two cells on which line recorders
are operating without disturbing this operation.

Other methods suggest themselves, but the final decision
is left to those who must operate this equipment.

f. **Laboratory Manifold**

Line recorders may be operated at times in the maintenance
shop and in the physics laboratory. At such times, a manifold simi-
lar to that of Figure II.1-20 is of use for mixing calibrating samples
and introducing them on unknown samples to the tube rack.

GLASS ENVELOPE

LEADS FOR CONNECTIONS
TO ELECTRODES.

MAGNET.

A.

J2

S

J1

GAS INLET.

MAGNET.

J3

A.

J5

G

PUMP LEAD.

SECTION "A-A"

KOVAR TO GLASS SEAL.

COPPER ANALYZER TUBE.

NICKEL TUBING

FLEXIBLE COUPLING.

MAGNETIC FIELD
CROSS SECTION.

ION COLLECTOR PLATE.

COLLECTOR LEAD.

TO PREAMPLIFIER.

FIGURE II.1-1

SCHEMATIC DRAWING OF LINE RECORDER
SPECTROMETER TUBE.

TITLE

			THE KELLEX CORP.	SCALE ___ DATE 7-27-44 AP
DESCRIPTION	DATE	CHECKED.		DR. J.P. TR.
REVISIONS				CKD. ___ NO. U-285 G

FLOW SHEET FOR LINE RECORDER TUBE RACK.
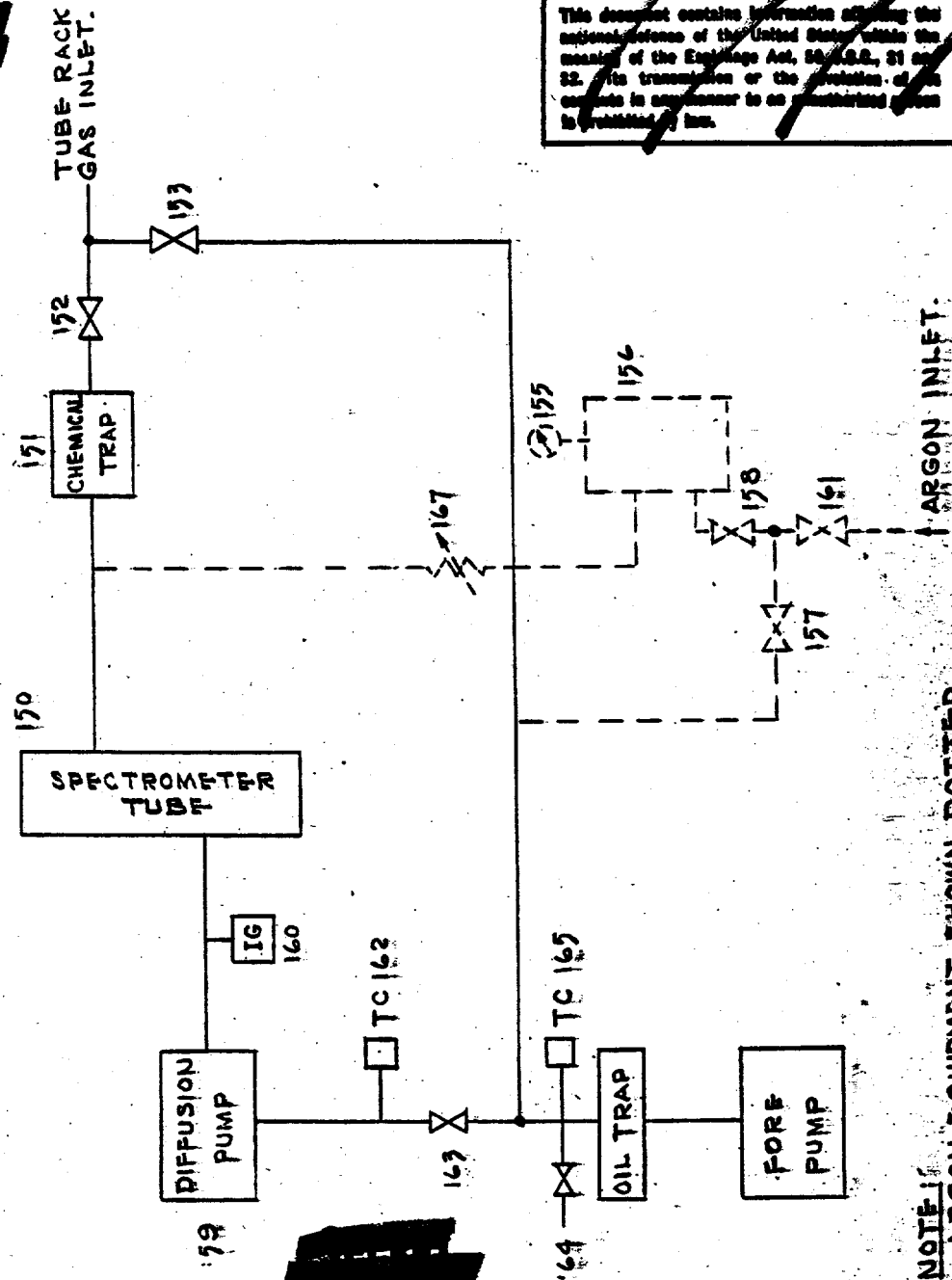
TITLE: FLOW SHEET FOR LINE RECORDER TUBE RACK.

FIGURE II.1-2

THE KELLEX CORP.

DESCRIPTION	DATE	CHECKED
REVISIONS		

SCALE _____ DATE _____ AP. _____
DR. _____ TR. _____
CKD. _____ No. _____ -D

NOTE:
ARGON EQUIPMENT SHOWN DOTTED.

MASTER CONTROL

115 V. MAINS

RECORDER

ION GAUGE

EMISSION REGULATOR

CONTROL PANEL

HIGH VOLTAGE SUPPLY

AMPLIFIER

VOLTAGE STABILIZER

PIRANI GAUGE CONTROL

PRE-AMPLIFIER

PIRANI GAUGE

GAS LEAD

SPECTROMETER TUBE

ION GAUGE

TO VACUUM

TITLE *ELECTRICAL CONNECTIONS BETWEEN COMPONENTS OF LINE RECORDER*

FIGURE II.1-3

DESCRIPTION	DATE	CHECKED	THE KELLEX CORP.
REVISIONS			
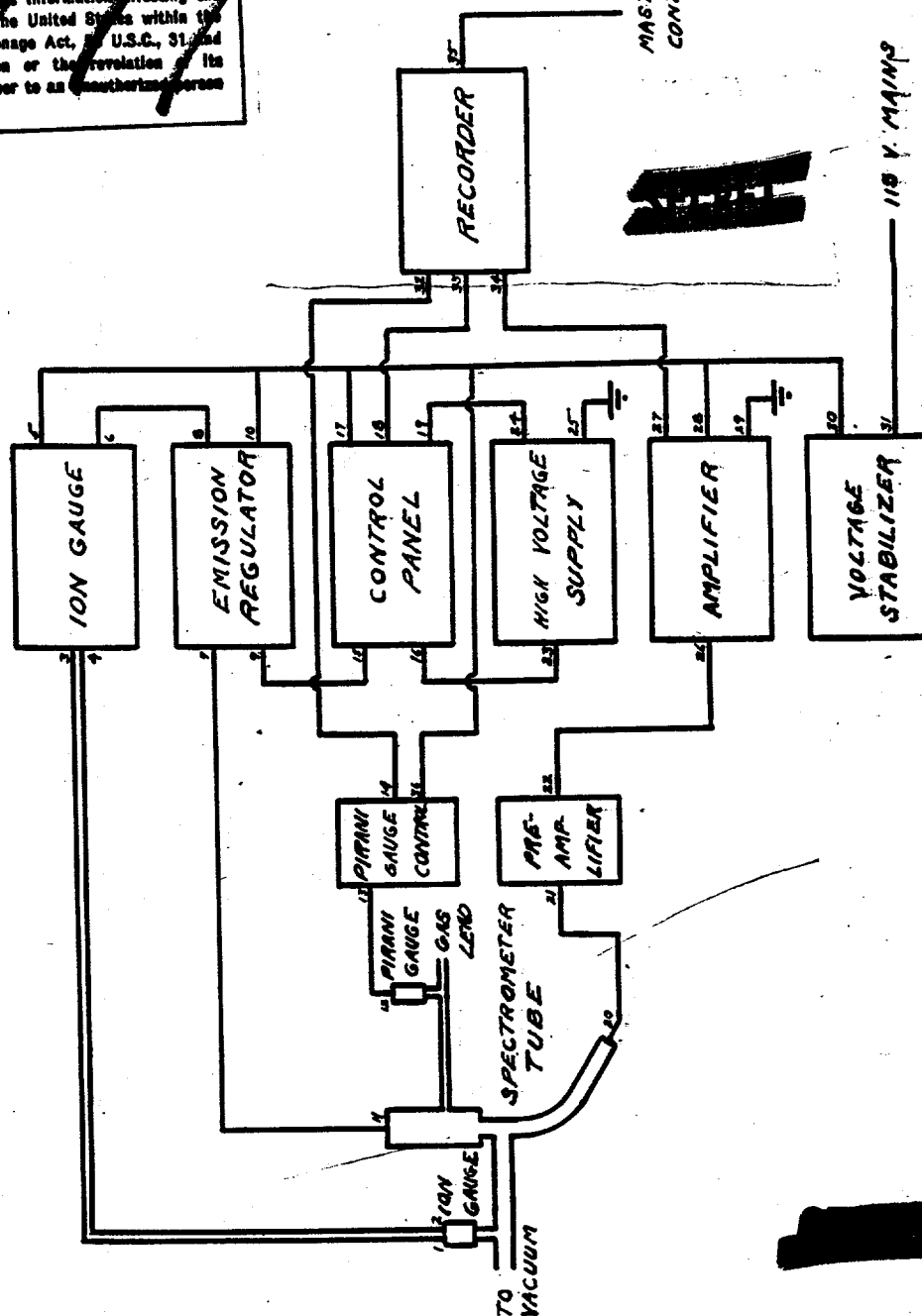
SCALE_____ DATE_____ AP._____

DR. _DD_   TR. _DD_

CKD._____ No._____ -D

SCALE FACTOR
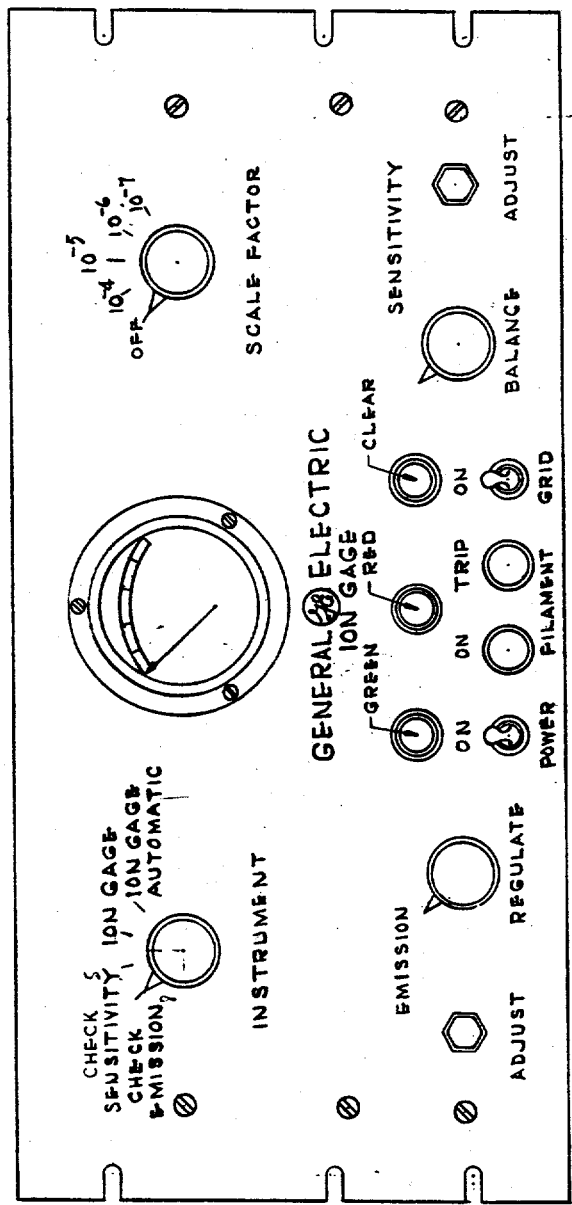
OFF 10^{-4} 10^{-5} 10^{-6} 10^{-7}

SENSITIVITY

BALANCE

ADJUST

GENERAL ELECTRIC
ION GAGE

GREEN
RED

CLEAR

ON
ON
TRIP
ON

POWER
FILAMENT
GRID

CHECK
SENSITIVITY
ION GAGE

CHECK
EMISSION
ION GAGE
AUTOMATIC

INSTRUMENT

EMISSION

ADJUST
REGULATE

FIGURE II.1-4

TITLE FRONT PANEL OF ION GAGE CIRCUIT.

THE KELLEX CORP.

SCALE
DATE
AP
DR.
TR.
No. _____ -G
CHD.

DESCRIPTION | DATE | CHECKED
REVISIONS

-24-

GENERAL ⊕ ELECTRIC

EMISSION REGULATOR

FOCUS J1&J2 COARSE

J4 FINE FOCUS

J3 FOCUS

J4 FOCUS

POWER ON. OFF.

FILAMENT ON. OFF.

EMISSION X4 OFF TRAP X1

INSTRUMENT

COARSE EMISSION FINE

REGULATE

FIGURE II.1-5

STRIP OF RECORDER CHART AS PRINTED BY
L & N MICROMAX RECORDER USED ON
A LINE RECORDER

NOTE: NOT TYPICAL PLANT PROGRAM

FIGURE II.1-6

FIGURE II.1-7

GENERAL ⓔ ELECTRIC
D.C. AMPLIFIER

CURRENT

OUTPUT

POWER — ON. — OFF.

BATTERY CHECK

FILAMENT — OPEN

BALANCE — INCREASE — FINE — INCREASE — MEDIUM — INCREASE — COARSE

V.8 V.7

A B C D
E F G H

X20 X10 X5 X2 X1
X50 X100 OFF

X50 X20 X10 X5 X2 X1 OFF X100 X200 X500 X1000

FIGURE II.1-8

TITLE: FRONT PANEL OF MAIN CONTROL

THE KELLEX CORP.
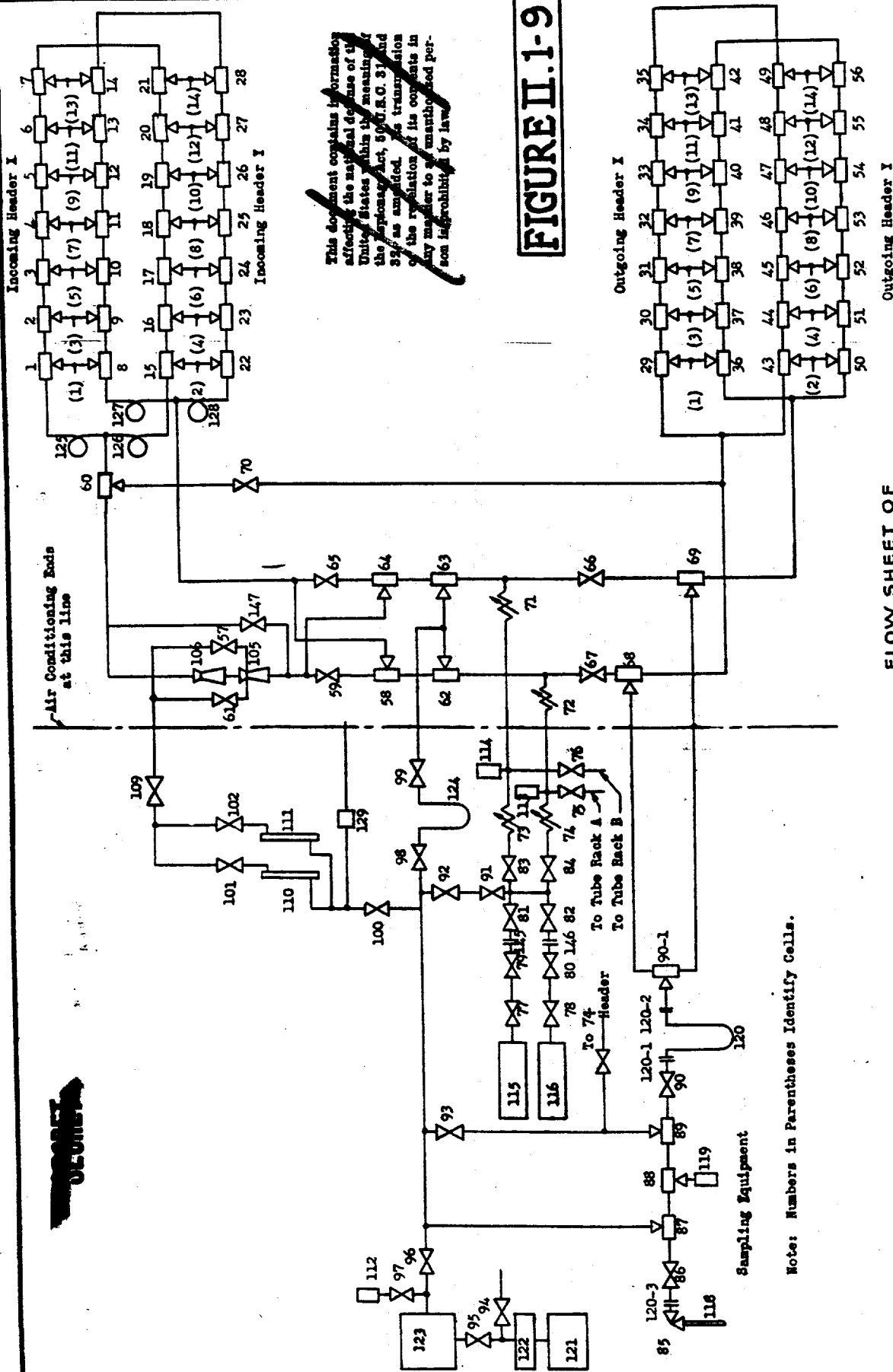
FIGURE II.1-9

FLOW SHEET OF
MANIFOLD ASSEMBLY

THE KELLEX CORP.

Note: Numbers in Parentheses Identify Cells.

GAS OUTLET

LEAK PLUG

JAW

LEAK CLAMP

CAPILLARY PLUG

CAPILLARY

LEAK TUBE

GAS INLET

Schematic Diagram of Gas
Flow Through the Leak

FIGURE II.1-10

SCALE ___ DATE ___ AP. ___
DR. ___ Tr. ___
CHD. ___ No. ___ -G

THE KELLEX CORP.

TITLE

DESCRIPTION	DATE	CHECKED
REVISIONS		

HANDLE

SHOE

JAW

LEAK

CLAMP

FIGURE II.1-11

TITLE *Adjustable Leak Clamp*

THE KELLEX CORP.

SCALE _____ AP. _____
DR. _____ Tr. _____
CHD. _____ No. ___-G

DESCRIPTION	DATE	CHECKED
REVISIONS		

BRIDGE CURRENT METER.

OUTPUT METERS.

BRIDGE CURRENT METER.

GENERAL ⊕ ELECTRIC
PIRANI GAGE.

BRIDGE CURRENT METER.

BRIDGE CURRENT

BALANCE

BALANCE

BRIDGE CURRENT

100   200

100   200

POWER
ON   OFF

POWER
ON   OFF

FIGURE II.1-13

MANIFOLD FLOW SHEET FOR
NORMAL OPERATION OF LINE RECORDERS

THE KELLEX CORP.

LEGEND:

——— GAS AT PLANT PRESSURE
— — GAS AT LOW PRESSURE
|||||||||| VACUUM

Note: Numbers in Parentheses Identify Cells.

Sampling Equipment

FIGURE II.14

TITLE MANIFOLD FLOW SHEET WHEN OBTAINING RESIDUALS FOR RACK-"A"

THE KELLEX CORP.

FIGURE II.1-15

MANIFOLD FLOW SHEET WHEN
CALIBRATING TUBE RACK "A" WITH STD SAMPLE.

THE KELLEX CORP.

LEGEND

GAS AT PLANT PRESSURE
GAS AT LOW PRESSURE
VACUUM

Sampling Equipment

Note: Numbers in Parentheses Identify Cells.

-35-

FIGURE II.1-16

MANIFOLD FLOW SHEET WHEN
CALIBRATING TUBE RACK "A" WITH AIR

THE KELLEX CORP.

LEGEND:
———— GAS AT PLANT PRESSURE
———— GAS AT LOW PRESSURE
|||||||||| VACUUM
—·—·— AIR FOR STATIC CALIBRATION

Note: Numbers in Parentheses Identify Cells.

Sampling Equipment

FIGURE II.1-17

MANIFOLD FLOW SHEET FOR DYNAMIC CALIBRATION OF TUBE RACK "A"

LEGEND
— GAS AT PLANT PRESSURE
— GAS AT LOW PRESSURE
.... VACUUM
—·—·— AIR FOR DYNAMIC CALIBRATION
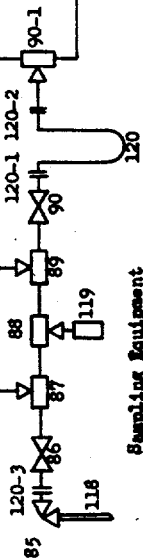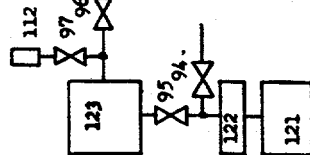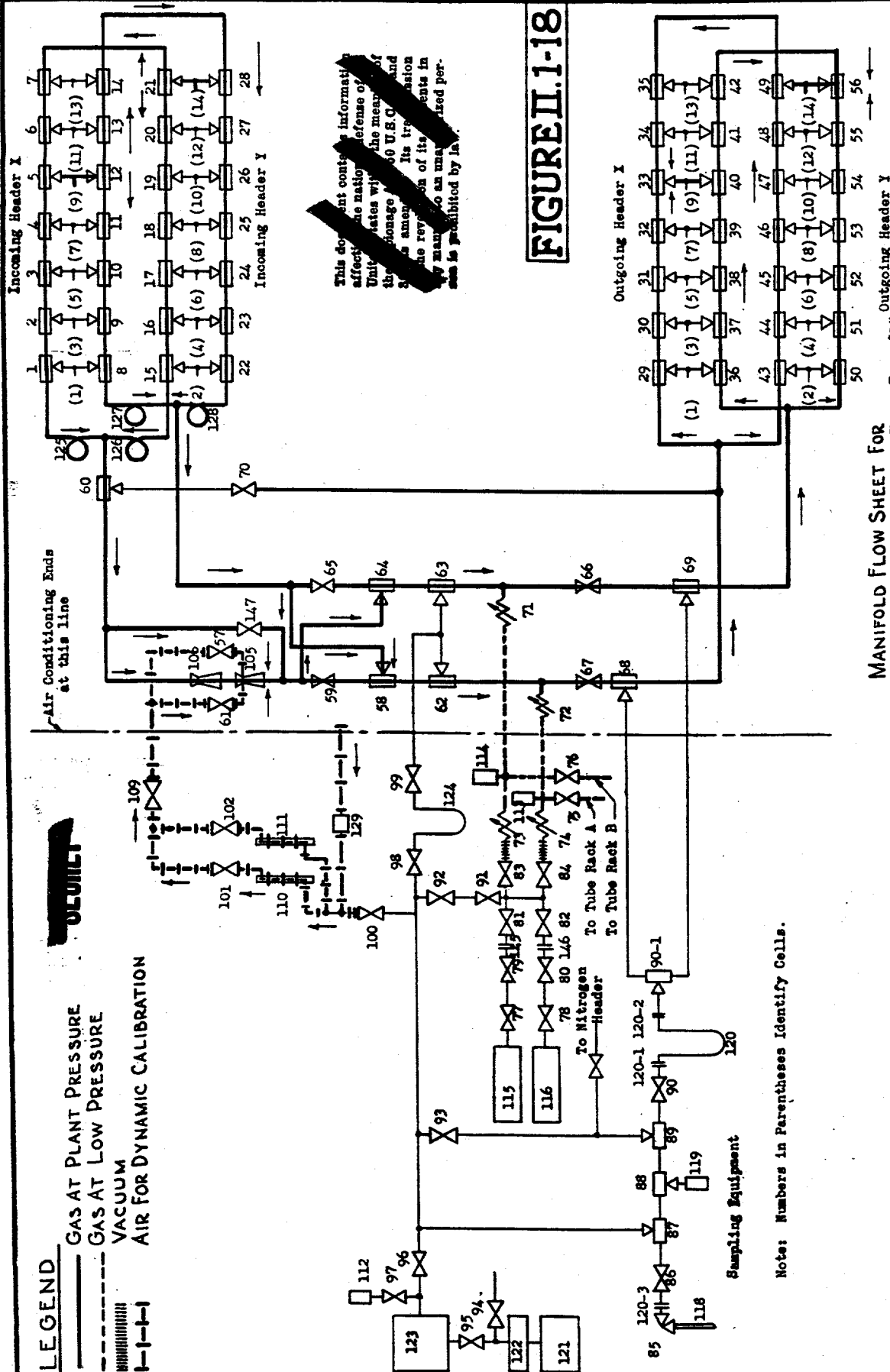
Note: Numbers in Parentheses Identify Cells.

THE KELLEX CORP.

FIGURE II.1-18

MANIFOLD FLOW SHEET FOR
DYNAMIC CALIBRATION OF TUBE RACK "B"

THE KELLEX CORP.
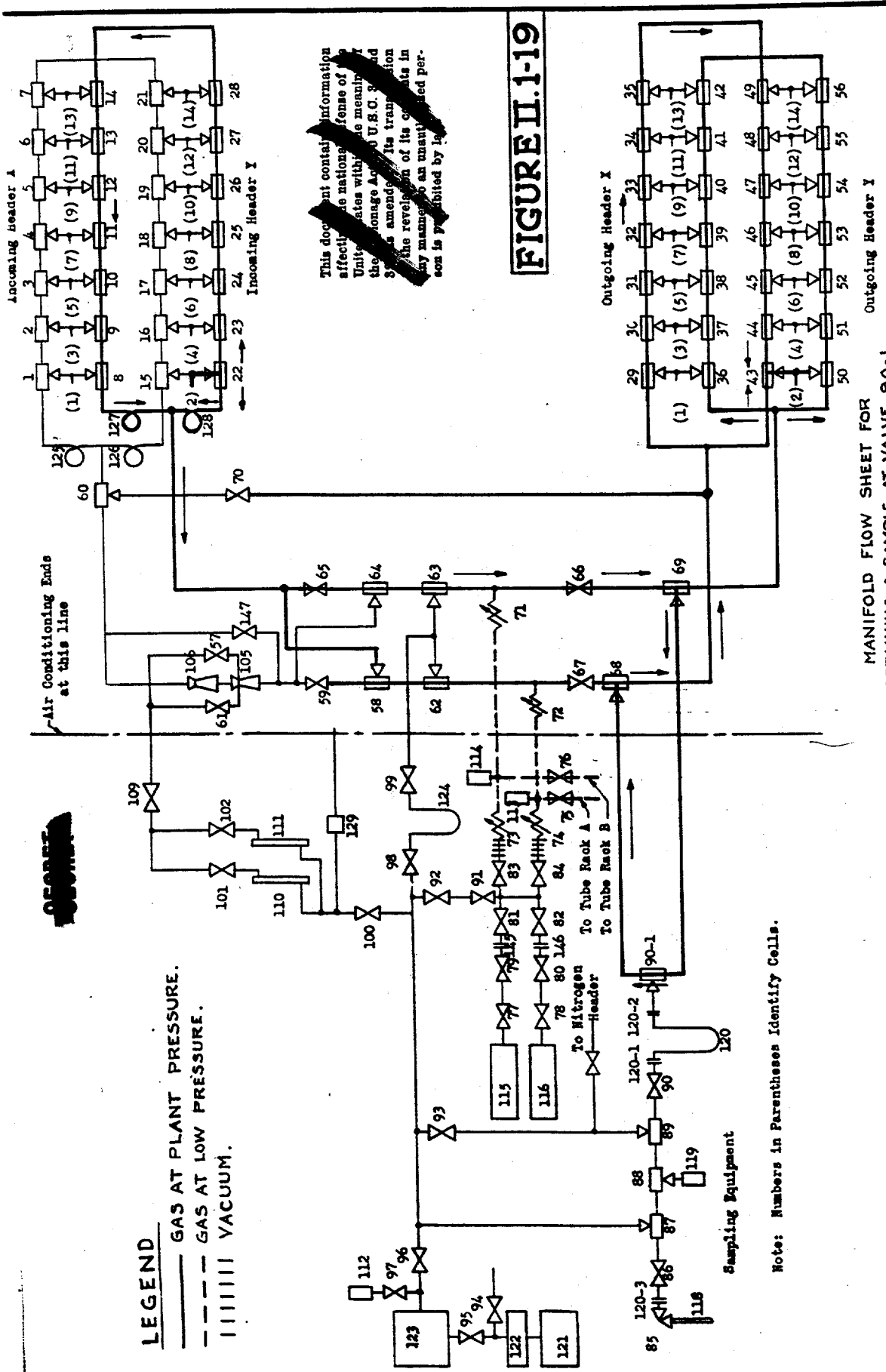
FIGURE II.1-19

MANIFOLD FLOW SHEET FOR
Title OBTAINING·A·SAMPLE AT VALVE 90-1.

THE KELLEX CORP.

LEGEND
——— GAS AT PLANT PRESSURE.
– – – GAS AT LOW PRESSURE.
|||||| VACUUM.

Sampling Equipment

Note: Numbers in Parentheses Identify Cells.

Air Conditioning Ends at this line

-39-
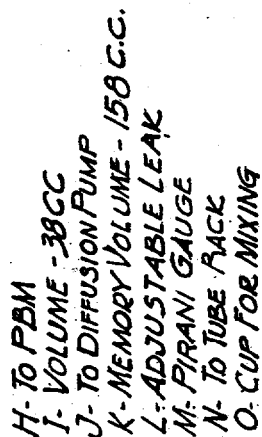
FIGURE II.1-20

A- MIXING BOTTLE - ONE LITER
B- 816 SUPPLY - 12 CC
C- 616 SUPPLY - 60CC
D- DRYING TUBE
E- CONN. FOR UNKNOWN SAMPLES
F & G - CALIBRATING BOTTLES - ONE LITER

H- TO PBM
I- VOLUME - 38CC
J- TO DIFFUSION PUMP
K- MEMORY VOLUME - 158 C.C.
L- ADJUSTABLE LEAK
M- PIRANI GAUGE
N- TO TUBE RACK
O- CUP FOR MIXING

TITLE: MIXING MANIFOLD FOR LINE RECORDER
No. 565

THE KELLEX CORP.

SCALE ___ DATE ___ AP. ___
DR. ___ TR. ___
CHD ___ No. ___ -G

REVISIONS
DESCRIPTION | DATE | CHECKED

2. Operation of the Line Recorder

a. Function of the Line Recorder in the K-25 Plant

For the proper operation of the K-25 plant, it is imperative that the composition of the process stream be known at all times and at many points throughout the plant. This knowledge is vital not only in determining process conditions but also in detecting any leaks as soon after formation as possible. It is desirable to measure the nitrogen, oxygen, 816, and 616 content of the process stream continuously and to check occasionally for the presence of such gases as N_2O and CC_2. Since a leak which is large enough to cause considerable harm may contribute only a few per cent to the 74 content of the process stream, it is desirable that the line recorder be able to distinguish changes of a few per cent in the gas composition. The composition may range from much less than one per cent to over seventy-five per cent 74. The range over which the 816 may vary is not nearly so large, but the problem of analysis is complicated by the fact that variations are small and are propagated slowly to the points of line recorder sampling.

It is desired that a continuous record be kept of the composition of the process stream at the end of each building and that provisions be made for measuring the composition of the process stream at each cell if such need should arise. The continuous analyses are intended to detect, primarily, an abnormal rate of inleakage as soon as it occurs, so that, if it be serious, immediate steps may be taken to combat the trouble. The check on the individual cells is intended so that the cell where the abnormal leakage is occuring may be located. In the event that the inleakage is so small as not to be detectable by means of increases in concentration during operation, leaks may frequently be located by isolating a single cell and determining the rate of pressure build up. An abnormal rate of build up then indicates abnormal inleakage.

A line recorder as received from the manufacturer is not capable of doing the above. It must first be assembled, started up, and calibrated. It is then ready to go into operation.

b. Assembly

It is not intended to discuss in this manual the manner in which the tube rack or electronic units for a line recorder are assembled. The assembly procedure is shown in detail in General Electric's reports on the line recorder, and the terms used are given in these reports. However, certain parts of the assembly procedure will have a definite effect on the final operation of the tube rack and are not straightforward. It is desired to emphasize here a few such points.

1. The trapezoidal pole faces should be accurately aligned in respect to the magnet yoke. The desired dimensions are as follows:

   a.- The horizontal faces of the trapezoids should be 2" below the center line of the pump lead and exactly parallel to the upper milled edge of the magnet yoke.

   b - The distance from the upper obtuse angle of the trapezoid should be exactly 6-7/8" from the outside milled surface of the base of the magnet yoke.

   After these adjustments have been made, the screws holding the trapezoids should be tightened and the trapezoids should not be disturbed at any subsequent time.

2. The Line Recorder tube should be placed in the pillow block and adjusted so that the plane of the copper analyzer is parallel to the faces of the trapezoids. The distance between the vertical center line of the copper analyzer, measured at the point where the pump lead is attached, and the large milled outside surface of the base of the magnet should be exactly 5-13/16". Inasmuch as the copper tubing is one inch in diameter, it would be more convenient to measure the distance from the base of the magnet to the inside edge of the vertical copper tube. This distance should be exactly 6-5/16". In measuring this distance, care should be taken to choose a part of the copper tube which is not bent or otherwise distorted. After these adjustments have been made, the tube should be mounted firmly in place and not disturbed at any later time.

3. Before the gas lead is connected to the tube, cut the lead from the Argon leak to the tube near the point where it ties into the gas lead and pinch and solder shut both ends of the cut. (It is at present not intended to use the Argon calibrating system and therefore it is to be removed from the equipment when it is to be assembled).

c. Starting-up Procedure for Line Recorder

It is assumed that the line recorder is connected to either a manifold assembly in the plant or to a laboratory manifold. In either case, the space behind the leak or leaks going to the tube rack is evacuated. (See, for example, the method of obtaining residuals described in Section II.1-e of this manual.)

All cable connections from the tube rack to the electronic units are assumed already made and the preamplifier can mounted and connected to the amplifier. Then, the steps in starting the line recorder into operation are listed below. (All equipment mentioned is either on relay rack, Part II-D, or tube rack shown in Figure II.1-2).

1. Turn on amplifier (Figure II.1-7).

2. Turn on fore pump. Valves 161 and 164 are shut, all others open. (Figure II.1-2)

3. When the thermocouple gages (162 and 165 on Figure II.1-2) indicate a vacuum, the pump heater is turned on. Water must at this time be flowing through the pump cooling jacket.

4. One-half hour or longer after a mercury beam forms in the diffusion pump and a black vacuum is obtained, liquid air is put on the cold trap and dry ice slush is put on the chemical trap.

5. Turn on ion gage, emission regulator, and high voltage supply power switches.

6. Ten minutes later, the ion gage filament is turned on, and the grid may be outgassed.

7. When pressure is less than 5×10^{-5} mm. of mercury, turn on the emission regulator and adjust the emission to 100 microamperes. Set acceleration voltage selector on main control panel to the manual position.

8. Adjust the source magnet by eye so that the center line of the poles coincides with a line parallel to the center line of the source box, but just above the lower face at the level of the apex of the filament hairpin. The south seeking pole of a compass should point toward the magnet pole on the filament end of the source box. Make minor adjustments in the position of the source magnet in order to maximize the trap current. The trap current should be at least 90% of the total emission. This should be obtained without misaligning the magnet a visible amount. If difficulty is found in obtaining sufficient trap current, it may indicate that the filament hairpin is not properly aligned or that something else is wrong. There is the remote possibility that the source magnet is not properly magnetized. Its field, when measured in the center of the air gap, should be 250 $\pm$ 50 gauss.

9. Mount the secondary electron suppressor magnet. The
    center of the air gap should be along a horizontal
    diameter of the collector housing and approximately
    1/4" toward the sylphon coupling from the point between
    the copper analyzer tube and the monel section. Its
    field should be in line with that of the main and
    source magnets.

10. Adjust the manual divider so that the measured shield to
    ground voltage is 1000 volts. Then J5 is adjusted so
    that the potential from J5 to ground is about 600 volts.
    The remainder of the focus voltages are set on the
    emission regulator panel as follows: The knob marked J1
    and J2 is set on step 6. This will place these electrodes
    at a potential of 108 volts below the shield. The knob
    marked J3 is set at step 7. Its potential will then be
    126 volts below the shield.

11. Magnetize the main magnet so that the mass 28 peak is
    collected when the accelerating voltage is 1050 ÷ 50 volts.
    The polarity of the main magnet should be such that when
    looking into the yoke with the poles toward one, the
    north seeking pole of a compass points at one's right
    when held near the magnet poles.

12. Turn on the Pirani gage circuit, wait until it reaches
    reasonable equilibrium (it will drop slowly towards
    zero after being turned on), adjust the Pirani gage
    zero to zero; now a small pressure of air is admitted
    behind the leak and the leak is adjusted until the
    Pirani reads about five scale divisions. (Ten millivolts).

13. Identify the various peaks in the machine. The large
    peaks at this time should be found at masses 14, 17,
    18, 28, 32, and 44. As an aid in identifying the
    peaks one notices first that the ratio of the 28 peak
    to the 32 peak and the ratio of the 18 peak to the 17
    peak are both nearly five to one, and second that the
    product of mass number by accelerating voltage is
    constant (allowing for some non-linarity in the voltage
    meter). If the 28 peak is not found in the voltage
    range specified in (11) above, the magnet strength is
    changed until this condition is rectified.

14. Reset the fine control for J1 in order to obtain
    a maximum signal for mass 28. The source magnet may
    now be adjusted very slightly to see if a better
    maximum can be obtained. However, in no case should
    such an adjustment be made at the expense of trap cur-
    rent, or in such a manner that the magnet is tilted
    more than a degree or two from horizontal. If the
    poles on the source magnet are unequal in strength
    it is possible that tilting the source magnet may
    improve matters. The proper remedy in this case is,
    however, to recharge the source magnet.

15. The next operation is to check the apparent resolution of the instrument. This is done by comparing the height of the valley between the 28 and 29 peaks with the height of the 29 peak. Without allowing the intensity of the 28 peak to drop to less than 95% of the value observed in (14), set J5 so that the valley is as low as possible. (These two requirements, maximum peak height and minimum valley, are conflicting. Hence the specification that no more than 5% of the peak height is to be sacrificed in obtaining a small valley.) Following the above procedure, the valley between the 28 and 29 peaks should not exceed 50% of the height of the 29 peak. If it exceeds 70%, it probably means that the tube is defective in some way. For an instrument in which the residual 28 and 29 peaks are small compared to the heights when air is flowing in, the ratio of the 28 peak to the 29 peak should be 110 or more.

16. Set the points on the fixed voltage divider to the proper settings for all the peaks except the mass 69 and the mass 30 peaks (unless there is some gas flowing into the tube rack giving rise to a peak, it is difficult to set the peak properly).

17. With air flowing in at such a rate as to make the Pirani gage read 50, the 14 peak should have a height of from two to four thousand divisions. Under these conditions, the ionization gage should indicate from 4 to 6×10^{-6}mm. above its residual reading. (This holds for the case where the total resistance to air at the Pirani gage is 365 seconds per liter, as will be true on all tube racks as delivered.)

The tube rack is now ready for operation. But, if 616 is run into the rack, one may anticipate a period in which all surfaces from the leaks to the chemical trap are being conditioned by the presence of the 616. In addition, the leads from the sample bottles to the calibrating leaks must be similarly conditioned. It will take a matter of several minutes to condition this region where the pressure is high, whereas in the vacuum side of the leak the process may take several hours.

The vacuum side of the leak, which includes the gas lines and the Pirani gage, may be conditioned by either admitting process stream or a calibrating sample to the tube rack. This should be done immediately after step (17) above in order that one may operate the line recorder as soon as possible.

d. Static Calibration

In order for the line recorder to be used as an analytical measuring instrument, it is necessary to calibrate the line recorder.

If the Pirani gage were a true flow measuring device, one calibration sample would be sufficient. Since this is not true, it is found that three calibration samples are necessary. One of these is ordinary room air. The other two are stored in the calibrating bottles built into the manifold assembly.

In the following discussion, it is assumed that the principle components of the gas being analyzed are 616, nitrogen, oxygen, and 816. The 816 content is assumed to rise to not more than a few per cent and other gases, such as SiF_4, CO_2, BF_3, and N_2O are assumed present to only a fraction of a per cent. The line recorder is presumed to be in good operating condition. Special attention is paid to the residuals, which should be within the limits set forth in Section II.4 of this manual.

The procedure outlined below is based upon a mode of operation of line recorders in which the gas flow through the leak is kept to a constant value, independent of gas composition or pressure behind the leak. This means, essentially, that the Pirani gage reading at which the line recorder is operated will have to be set in accordance with the gas composition, since the Pirani gage reading for constant flow through the leak varies with gas composition.

In addition, use is made of the fact that the line recorder output for a given sample can be varied by a change of emission in order to make all line recorders read in the same manner for the mass 28 peak. It will then be found that all line recorders will read nearly the same for all other peaks. The sensitivity for the 28 peak to which all the line recorders are to be adjusted is indicated in the table below:

Sensitivity Shunt Setting	% N_2 per Scale Division
1	0.002
2	0.004
5	0.01
10	0.02
20	0.04
50	0.1
100	0.2

The method of using the three calibration samples to determine first at what emission the line recorder is to be operated to obtain the sensitivity for the 28 peak indicated in the above table and second to determine in what manner the Pirani gage reading is to be varied with the heights of the various peaks in order to keep the flow through the leak constant, is discussed below. The three samples used are:

1. Between 5 and 10% air, remainder 616.

2. One hundred per cent air.

3. Between 5 and 10% air, about 2% 816, remainder 616.

The first calibration sample is admitted to the tube rack. If this is the first time that any of the spaces which are seen by the sample during this process come into contact with 616 since the last time the spaces were exposed to moist air, it is necessary to use caution that the sample is not contaminated due to the reaction with the surfaces. In order to prevent this, all such surfaces may be conditioned by admitting the sample, shutting the valve on the sample bottle immediately, and allowing the gas thus admitted to remain in contact with the surfaces being conditioned for several minutes, after which this gas is pumped out and a fresh sample admitted to the tube rack.

After the sample is admitted to the tube rack (it is assumed that there is a vacuum behind the other leak when using the manifold assembly), the leak is adjusted until the Pirani gage reading prints at 50 on the recorder scale. Then the emission is adjusted until the 28 peak prints at a value that corresponds to the per cent nitrogen in the sample in accordance with the previous table. Thus, for a sample containing 10% air, 90% 616, the per cent nitrogen is 7.8. Hence, the emission is adjusted until the 28 peak prints at 78 on shunt 50. In general, the emission will be between 100 and 200 microamperes, with a lower emission corresponding to a more sensitive line recorder. Once set in this manner, the emission is not varied until the next time the rack is calibrated. If the emission should vary from the amount here, as determined by reading the emission meter, it may be set to the proper value with the meter.

It may be pointed out that in general the peak heights will be nearly proportional to the Pirani gage reading, so that if the Pirani gage were set at 49 instead of 50 when the emission was adjusted, the peak should have been adjusted not to 78 on 50 but to 2% less than this or 76.4 on 50.

The second sample admitted to the tube rack might well be the 100% air. This will enable the determination of how the

Pirani gage reading is to be varied to compensate for the oxygen (measured by the 32 peak) and for the nitrogen (measured by the 14 peak, or, when it is on scale; by the 28 peak) present in the sample.

After the sample is admitted to the rack, the leak is adjusted until the 14 peak (the 28 peak will be off scale) reads the proper value, thus indicating that the flow through the leak is the same as it was for the first sample. By the proper value, one means that the ratio of the 14 peak for 100% air to the 14 peak for the first sample should equal the corresponding ratio for the per cents nitrogen in the samples. Thus, in the case where the first sample contains 10% air, the 14 peak for 100% air should be ten times as great as the 14 peak for the 10% air sample.

The Pirani reading will, in general, not be 50 when the 14 peak is adjusted to the proper value. This deviation from 50 represents the amount that the Pirani gage reading must be changed to keep the flow constant when the gas composition is 100% air. For intermediate amounts of air the deviation from 50 should be proportionately less. For convenience, it is recommended that a graph such as that shown in Figure II.2-1 be drawn from the data obtained from the first two calibration samples. If the 32 peak is off scale for the second sample, one uses the fact that the ratio of the 32 peaks for this sample and the first sample is the same as the ratio of the amounts of oxygen in the samples. The Pirani gage correction for oxygen and nitrogen in any succeeding sample may then be obtained directly from this graph. In plotting the graphs, it is assumed that oxygen and nitrogen contribute to the deviation in direct proportion to their abundance in the calibration sample. To use the graph in obtaining the correct Pirani reading on an unknown sample, the Pirani is first set at about 50 and then, from the 14 and 32 peak heights in conjunction with the graph, the Pirani correction is determined by adding together the individual corrections for oxygen and nitrogen. The correction is now added to 50 and the leak adjusted until the Pirani reads the corrected value. It will be found that the 14 and 32 peaks change with this adjustment, which in turn changes very slightly the correct operating value for the Pirani. This latter change may usually be neglected. It was endeavored, during design of the line recorder, to make the necessary Pirani correction due to air as small as possible. As a result, the corrections for oxygen and nitrogen will be negligible when the total oxygen plus nitrogen content of the sample is below 20%.

The third sample to be admitted to the tube rack, sample 2 above, is used to determine how the Pirani gage reading is varied to keep the gas flow constant when a sample contains 316. After the sample is admitted, the leak is adjusted until the 28

peak reads the proper value (for a sample with 10% air. 2% 816, 88% 616 this is 78 on shunt 50) and the value of the Pirani reading noted. The graph of Figure II.2-2 is then constructed.

The method of using the graphs of Figures II.2-1 and II.2-2 **is then as follows:**

1. The gas being analyzed is admitted to the tube rack and the leak set so the Pirani reads approximately 50.

2. The 14, 32, and 69 peaks are noted.

3. The Pirani gage corrections due to the 14 and 32 peaks, as obtained from A & B of Figure II.2-1, are summed and added to the Pirani gage reading as given by Figure II.2-2 for the 69 peak measured.

4. The leak is so set that the Pirani reads the value given in step 3.

In many cases (less than 20% oxygen plus nitrogen) it will be found that the effect of the 14 and 32 peaks as given by A & B of Figure II.2-1 may be neglected and the correct Pirani reading taken directly from Figure II.2-2 by use of the 69 peak.

The following example of a typical calibration may serve to clarify the procedure.

1. A sample consisting of 5% air and 95% 616 was admitted to the line recorder.

2. The leak was adjusted until the Pirani gage read about 50 and the following data recorded:

Pirani	14 Peak	28 Peak	32 Peak	69 Peak
51	146	1460	292	1

3. To conform with the sensitivity indicated in the table already presented in this section, the 28 peak for a 5% air sample should, with a Pirani reading of 51, be

$$\frac{51}{50} \times \frac{0.78 \times 5.00}{0.002} = 1990$$

The emission was therefore increased until the 28 peak read 1990. The value of the emission was carefully noted and recorded and the following data obtained:

Pirani	14 Peak	28 Peak	32 Peak	69 Peak
51	199	1990	398	1

4. The value of emission as obtained in step 3 is maintained
until the line recorder is recalibrated. For convenience,
a Pirani gage reading of 50 has been chosen as the base
from which to apply corrections. The data in step 3 was
therefore converted to a Pirani reading of 50 by the
multiplication of each peak by 50/51.

Pirani	14 Peak	28 Peak	32 Peak	69 Peak
50	195	1950	390	1

These data were plotted as point A in Figure II.2-1. One
uses the same data to calculate the calibration constants
for oxygen and nitrogen.

$$\% \text{ Nitrogen} = \frac{5.00 \times 0.78}{1950} \times 28 \text{ peak} = 0.002 \times 28 \text{ peak}$$

$$\% \text{ Nitrogen} = \frac{5.00 \times 0.78}{195} \times 14 \text{ peak} = 0.02 \times 14 \text{ peak}$$

$$\% \text{ Oxygen} = \frac{5.00 \times 0.21}{390} \times 32 \text{ peak} = 0.00269 \times 32 \text{ peak}$$

The value thus found for the calibration constant for the 28
peak agrees, as it must if the calibration is properly
carried out, with the value given in the previous table of
sensitivities for the 28 peak for sensitivity shunt 1.

5. The sample was next removed and replaced with a sample
of 100% air. The proper value for the 14 peak was
determined using the data of step 4:

$$14 \text{ peak} = \frac{100 \times 0.78}{0.02} = 3900$$

The leak was adjusted until the 14 peak read 3900 and the
following data recorded:

Pirani	14 Peak	28 Peak	32 Peak	69 Peak
48	3900	off scale	7800	1

The deviation of the Pirani gage reading from 50 for this
sample is the Pirani gage correction for 100% air. The
correction (- 2) is divided between the oxygen and nitrogen
in proportion to their relative abundance in air, 0.21/0.78.
This gives rise to point B of Figure II.2-1.

6. The 100% air sample was pumped out and replaced by the third sample, which consisted of 2% 816, 10% air, and 88% 616. The proper value for the 14 peak for this sample is:

$$14 \text{ peak} = \frac{10.0 \times 0.78}{0.02} = 390$$

The leak was adjusted until the 14 peak read this value and the following data obtained:

Pirani	14 Peak	28 Peak	32 Peak	69 Peak
55	390	3900	780	4800

From these data, point C of Figure II.2-2 was plotted. Connecting this point with point A (which is always the same), provided the means of using the graph for other amounts of 816. One also uses the above data to obtain the calibration constant for 816.

$$\%816 = \frac{2}{4800} \text{ x peak} = 0.000417 \times 69 \text{ peak}$$

e. Plant Operation

Once the line recorder is calibrated, it is ready to be connected to the plant stream. The valve turning procedure necessary to accomplish this follows directly from the description of the manifold assembly given in Section II.1 of this manual. Once the proper valves have been turned, the tube rack is connected to the plant stream and ready for operation. The steps in obtaining an analysis are as follows:

1. Adjust the leak so that the Pirani gage reads approximately 50 scale divisions.

2. Using Figures II.2-1 and II.2-2 and the recorded heights of the 14, 32, and 69 peaks, determine the proper Pirani reading for the process stream in the cell being analyzed.

3. Reset the leak so that the Pirani reads the correct value.

The nitrogen content of the process stream is now given directly according to the table of Section II.2-d, according to the calibration constant calculated in Section II.2-d. The calibration constants for oxygen and 816 have also been found in Section II.2-d, for a particular line recorder. For any other instrument, these calibration constants are found in the same way during the calibration procedure.

An example of the analysis of an unknown sample (pre-
sumably the process stream) upon the machine whose calibration
was discussed in Section II.2-d is given here.

1. The unknown sample is admitted to the tube rack and
the leak adjusted so that the Pirani reads approxi-
mately 50. The following data are obtained:

Pirani	14 Peak	28 Peak	32 Peak	69 Peak
49	301	3010	180	720

2. From the 14 and 32 peaks in conjunction with Figure II.2-1,
the Pirani correction is found to be

$$(-0.03) + (+0.03) = 0$$

This correction (in this case, as in many others, it
is negligible) is added to the Pirani gage reading
determined from Figure II.2-2 for the 69 peak of the
sample. The resulting Pirani gage reading turns out
to be 50.7.

3. Upon readjusting the leak until the Pirani reads 50.7,
one obtains the following data for the sample:

Pirani	14 Peak	28 Peak	32 Peak	69 Peak
50.7	311	3110	186	744

Upon checking the results of step 2, one finds that the
change in peak heights between steps 1 and 3 is in-
sufficient to make any significant change in the proper
Pirani gage reading.

4. Using the calibration constants previously determined,
the composition of the sample is:

% nitrogen = 0.002 x 3110 = 6.2%

% Nitrogen = 0.02 x 311 = 6.2%

% Oxygen = 0.00269 x 186 = 0.50%

% 816 = 0.000417 x 744 = 0.31%

Once the line recorder is operating upon the process
stream, the difficult problem is, not to obtain analyses, which
is done automatically, but to keep the machine operating properly

and determine when it has ceased to do so or when, for some reason, the calibration has changed. For proper operation of the tube rack, the liquid air and dry ice slush bottles must be kept properly filled and the cooling water must be flowing into the pump jacket. In addition to this, the fore pump and the diffusion pump heater must both be operating properly. Not only is the correct operation of the above almost self evident, but various alarm devices have been included on the plant tube racks to tell when something is not operating correctly.

Any deviation from correct operation of the electronic units may show up in the manner in which the recorder chart is printed. If the points printed are not in straight vertical lines but scatter about some mean in an apparently random fashion something is wrong. If the points printed for any one component seem to divide themselves more or less regularly along two lines, the chances are that the emission regulator functions incorrectly. In addition, the output meter on the amplifier should be steady when the line recorder is adjusted to any peak or to the amplifier zero.

The value of the emission should hold steady at the setting determined during static calibration. If it should drift slightly, it should be reset. If, however, the emission changes quite often, or whenever the concentration of the gas flowing into the tube rack changes appreciably, then the emission regulator is not regulating and is therefore not satisfactory.

A convenient check upon the possibility of the calibration of a machine having changed is the line recorder analysis for a hundred per cent air. If this analysis nearly checks, but not quite, when the Pirani is set at the value determined from Figure II.2-1, the emission may be adjusted to compensate for the slight change. If the analysis misses the known composition of the air by several per cent or more, it would appear necessary to recalibrate the line recorder.

The dynamic calibration procedure, described briefly in the next section, is expected to provide an even more convenient method of checking the line recorder calibration.

f. Dynamic Calibration

The dynamic calibration procedure is based upon the idea of adding a known quantity of air to the process stream and seeing whether the 28 peak and the 32 peak increase accordingly. In order to do this, it is necessary to measure the main stream flow, which is done with the venturi and pressure and temperature measuring equipment included in the manifold. The air flow is measured with a rotameter. The procedure for the valve turning part of this operation has been described in Section II.1.

The analysis of the results of dynamic calibration will not be discussed here but will be the subject of a separate report (This report will be prepared by Kellex at some later date.) which will include charts or tables to simplify the flow calculations. It is unfortunate that the manner in which the dynamic calibration method ties in with the flow of process stream in the sample lines has made it impossible to test the method in the laboratory, so that the final experience necessary to determine how to operate the equipment will have to be obtained in the field.

However, if the dynamic calibration equipment works as anticipated, one may expect that it will relegate the static calibrating equipment to a relatively infrequently used master standard. The ease of using the dynamic equipment is such that it might well be used once every twenty-four hours, thus giving a much more frequent check upon line recorder calibration than is feasible with the static calibration equipment.

g. Laboratory Operation and Sample Preparation

To permit unknown or calibration samples to be admitted to the tube rack through the leak, a manifold like that shown in Figure II.1-20 is used. To admit a sample for analysis, the sample bottle is soldered onto the manifold at any convenient location (one provided for that purpose on the manifold) and the joint between the bottle and the manifold is evacuated with the diffusion pump. The joint is then leak tested, using the tube rack for this purpose. The manifold is evacuated so that the line recorder gives a satisfactory residual reading on the 28 peak and the pump line is then shut off. The valve between the sample bottle and the remainder of the manifold has, of course, been open. If a leak is present, the line recorder will show a steady rise in the 28 peak due to the rising air pressure behind the leak. If no leak is present, the tubing in which the soldered joint was made is fluorinated by admitting 616 from the 616 supply can at a pressure of several cms. of mercury. This 616 should be left in place for five minutes and may then be pumped out. If the line recorder shows a reasonably low residual, the valve of the sample can is opened, admitting the sample to the tube rack.

The manifold of Figure II.1-20 may be used for the mixing of calibration samples. For this purpose a 616 supply, an 816 supply, and an air supply are built into the manifold. The sample is prepared in the mixing bottle, the composition of the sample being determined by means of the pressures of the various constituents admitted to the bottle. Pressures in the manifold are measured by means of a Taylor 0-2 psi absolute PBM transmitter, the output of which is used to actuate a mercury manometer. The output pressure of the transmitter is 7.5 times the input, so that 7.5 c.m. mercury reading on the manometer corresponds to 100 cm. of mercury pressure in the manifold. In the following discussion of mixing, numerical pressure values will be given in cm. mercury of the transmitter output.

Before a sample can be mixed, the 616 and 816 bottles must be filled. To fill the 816 bottle, the soldered cap on the side tube is removed and liquid 816 poured in. The bottle is frozen down in liquid nitrogen and the cap is soldered on the bottle. Then the valve connecting the bottle to the manifold is opened and the air above the solid 816 in the bottle is pumped off through the manifold diffusion pump. The valve on the bottle is shut and the bottle is allowed to warm up.

To fill the 616 bottle, diffusional transfer is used. The drying tube on the manifold is replaced by a 616 supply. The 616 bottle, the manifold, and the connection to the 616 supply can be evacuated. The pump valve is closed, the 616 supply can valve opened, and the 616 bottle immersed in liquid nitrogen. Transfer will take place. While 616 is transferring, shutting off the supply can will cause the pressure in the manifold to drop. When the pressure no longer drops to a fraction of a centimeter of mercury when this is done, either the bottle is full or the manifold contains non-condensible gases. These should be pumped off and the process repeated until it seems likely that the transfer process is completed. Then the 616 bottle valve is shut as is the 616 supply can. The supply can is removed and the drying tube replaced.

The 616 supply may contain excessive amounts of HF, in which case it may be purified by freezing the 616 down in dry ice slush and pumping above it, then warming up, repeating the process several times.

Once the 616 and 816 bottles are filled, samples may be mixed. To mix a sample containing by volume A% air, B% 816, remainder 616, the preliminary calculations are:

1. Choose a value for the total sample pressure, P_t.

2. The air pressure in the bottle will then be

$$P_{air} = \frac{A}{100} P_t$$

3. The partial pressure of 816 in the bottle will be

$$P_{816} = \frac{B}{100} P_t$$

4. The pressure of 816 admitted to the manifold will then have to be

$$P_{816} + P_{air}$$

Of the pressure of 816 admitted to the manifold,
a part must balance the pressure of the air already
in the bottle. Only the remainder forces the 816
into the mixing bottle.

5. The total pressure in the bottle is then brought up to
P_t with 616.

It is desirable to admit the smallest component to the
mixing bottle first, so that if there is more air than 816 in a
sample, the order above is reversed. Some sample computations
follow:

TABLE II

Row	Sample No.	1	2	3
(1)	% Air	30	20	5
(2)	% 816	20	30	1
(3)	% 616	50	50	94
(4)	P_t	60	60	60
(5)	Component Admitted First	816	Air	816
(6)	Partial Press. In Bottle	12	12	0.60
(7)	Component Admitted Second	Air	816	Air
(8)	Partial Press. In Bottle	18	18	3.0
(9)	Pressure in Manifold	30	30	3.6

In order to mix sample No. 1 in the above table, the proce-
dure is:

1. Evacuate manifold and mixing bottle.

2. Admit 816 to the manifold and mixing bottle to
   pressure in row (6), 12 cm Hg.

3. Close off mixing bottle and pump out manifold.

4. Admit air to manifold adjusting air valve so that
   air is slowly bled into the manifold. Adjust air
   pressure so that it is above 12 cm and below row (9)
   pressure of 30 cm.

5. Open valve to admit air through capillary tube into mixing bottle allowing air to flow simultaneously into manifold and carefully adjusting air inlet valve until total pressure in manifold reaches 30 cm Hg with air inlet shut off.

6. Close valve to sample bottle before the 816 has time to diffuse back through the capillary into the manifold. The presence of the capillary is intended to slow this back diffusion so that accurate samples may be mixed.

7. Admit 616 from the supply bottle to the manifold bringing the manifold pressure up to more than 30 cm and less than P_t.

8. Open the valve to the capillary on the mixing bottle and simultaneously govern the 616 supply so that eventually the manifold pressure reaches P_t with the 616 supply shut off.

9. Close off the mixing bottle before the air and 816 in the bottle can diffuse back into the manifold. Pump out the manifold.

10. Use a magnet to raise and lower the magnetic mixer inside the bottle. Bring the mixer to the top and let it drop a dozen or so times.

11. Throw away a bit of the sample to clear out any poorly mixed sample that may have been trapped in the 3/8" diameter connecting tube on the mixing bottle. To do this, admit part of the sample to the evacuated manifold. Close off the bottle and pump out the manifold.

The sample is now mixed and ready to admit to the tube rack or to be transferred to a bottle of some sort for storage.

A glance at sample No. 3 in Table II will show that the above procedure will lead to rather inaccurate results when the sample contains only small amounts of air or 816 since then the partial pressure of the air or 816 is small and hard to measure accurately. This difficulty can be removed if the pressure is measured while the gas is in a small volume and subsequently the gas is expanded into the mixing bottle. The ratio of volumes occupied by the gas before and after expansion must be known. A calculation form for this type of mixing is indicated in Table III. Either the 816 or the air or both may be expanded in this manner. The ratio of the volumes for which Table III is calculated is 1/6.9. The small volume used is the manifold plus pressure gage.

TABLE III

Row	Sample No.	4	5	6	7
(1)	% Air	2	2	20	20
(2)	% 816	2	20	2	30
(3)	% 616	96	78	78	50
(4)	P_t	60	60	60	60
(5)	Component Admitted First	Air	Air	816	Air
(6)	Partial Press. In Bottle	1.20	1.20	1.20	12.0
(7)	Pressure Before Expansion	8.28	8.28	8.28	----
(8)	Component Admitted Second	816	816	Air	816
(9)	Partial Press. In Bottle	1.20	12.0	12.0	18.0
(10)	6.9 x Part. Press. In Bottle	8.28	---	---	----
(11)	Pressure in Manifold	9.48	13.2	13.2	30.0

It may be noted that for sample No. 4, both 816 and air are expanded into the bottle rather than admitted directly; for sample No. 5, the air is expanded and the 816 admitted directly; for sample No. 6, the 816 is expanded; for sample No. 7, both components are admitted directly to the bottle.

Sample No. 4 would be mixed as follows:

1. Evacuate manifold and mixing bottle.

2. Admit air to manifold to pressure in row (7), 8.28 cm, with mixing bottle closed off. Open valve to permit air to expand into mixing bottle.

3. Shut off mixing bottle and pump out manifold.

4. Admit 816 to manifold at pressure in row (11), 9.48 cm, with mixing bottle closed off.

5. Open valve to permit 816 to expand into mixing bottle through capillary.

6. Close valve to mixing bottle after approximately
ten seconds and pump out the manifold.

7. Admit 616 from supply bottle to the manifold,
bringing the manifold pressure up to 10 cm.
or more, but less than P_t.

8 - 11 Same as in previous set of mixing instructions.

The mixing of other samples follow a similar procedure.
Variations of the method may be desirable in special cases, as
when many samples are to be mixed with the same composition. For
this purpose, additional volumes are included in the mixing mani-
fold. For samples with small amounts of any component, it may be
desirable to use double expansion or a small volume to expand
from in single expansion.

The "memory" volume is used to store one sample during
its analysis while the next one is being mixed. The two calibra-
ting bottles are used to save calibrating samples from one day
to the next so that one may use the stored samples for many
calibrations rather than mix fresh ones every time.

CORRECTION TO PIRANI GAGE READING
FOR NITROGEN AND OXYGEN
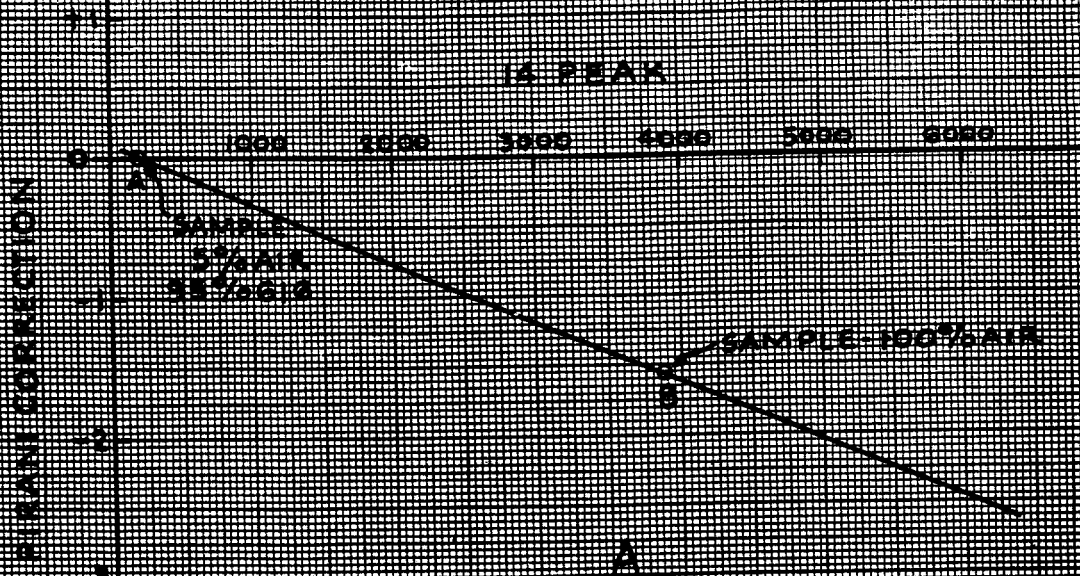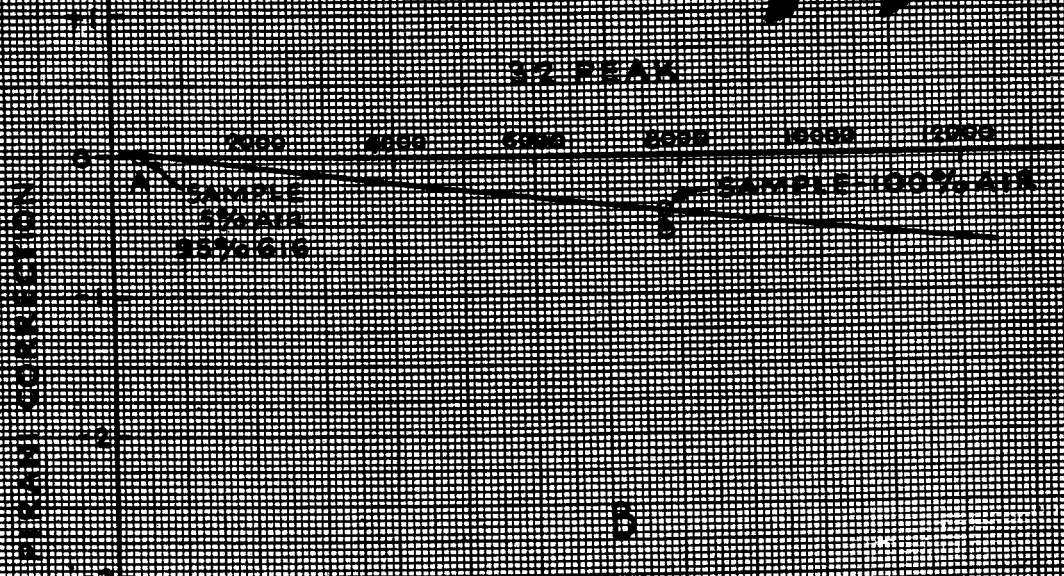
FIGURE II.2-1

DETERMINATION OF PIRANI GAGE
READING FOR SAMPLES CONTAINING B₆
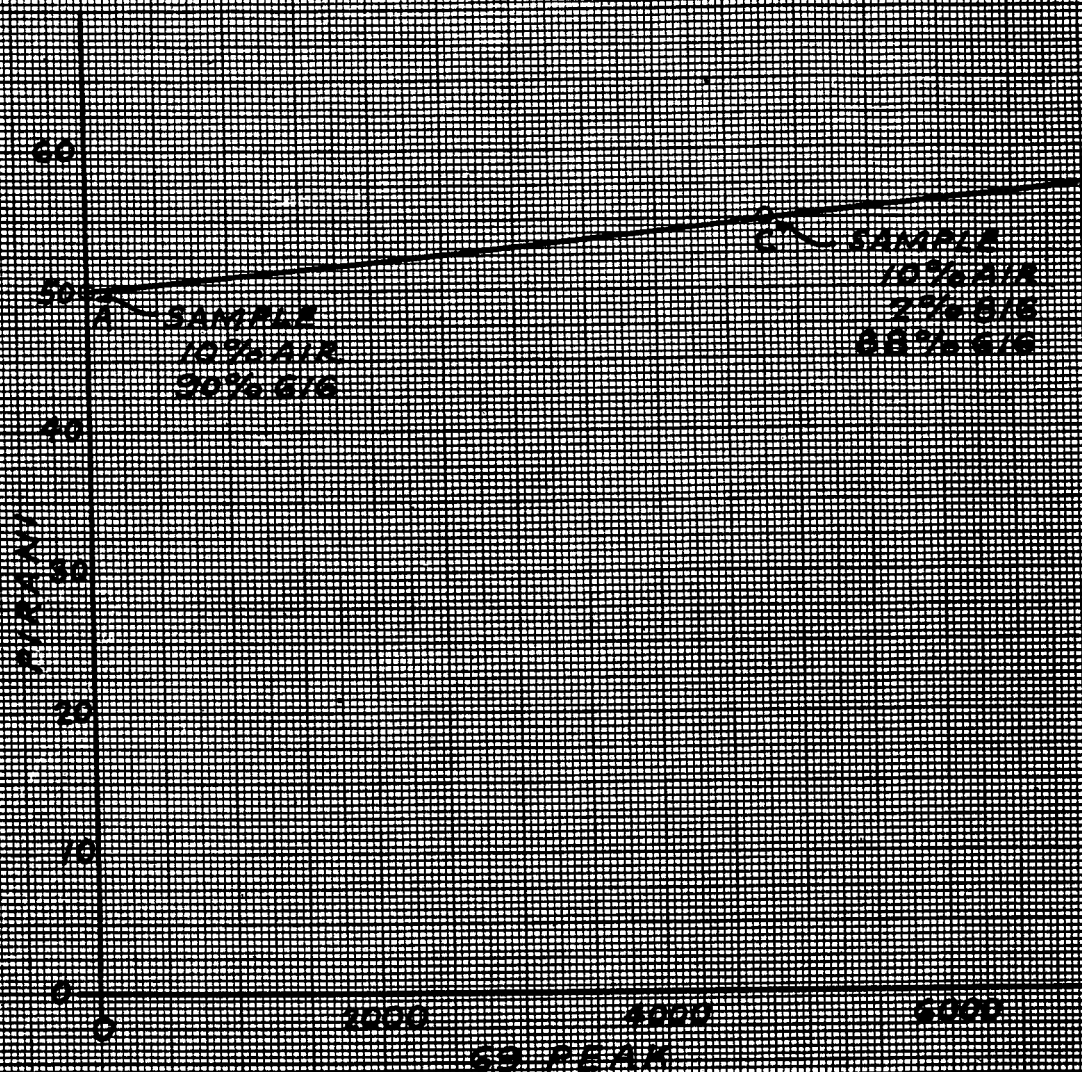
FIGURE II.2-2

3. Theory of Line Recorder Operation

a. Analysis of Gas Mixtures Not Containing C-616

A gas entering the spectrometer tube indicates its presence by producing one or more peaks in the line recorder spectrum. For example, carbon dioxide produces peaks corresponding to masses 12, 14, 16, 28, 32, and 44. These peaks are due to the various positively charged fragments of CO_2 produced by the ionizing electrons in the source.

The peaks are measured by the positive ion currents to the collector plate. The collector current flows through a resistance of 5×10^9 ohms and the voltage drop across this resistance is impressed on the input of a negative feed-back amplifier. Since the output and input voltages are for all practical purposes numerically equal, the output meter reads the voltage drop produced by the ion current. For convenience, the output is measured in scale units, where each unit represents two millivolts or $0.002/(5 \times 10^9) = 4 \times 10^{-13}$ amperes ion current. The self-balancing multi-point recording potentiometer connected in parallel with the amplifier output meter employes the same unit of measure. In both cases the output is determined by multiplying the scale reading by the scale multiplying factor. The resultant product is called the peak height, signal, or peak intensity in this report.

The intensity of the peaks depends upon many factors, including the rate of flow into the system of the gas producing the peaks. In the analysis given here it will be assumed that all factors affecting peak height are maintained constant except the rate of gas flow. In this case, the peak height is proportional to gas inflow; that is

$$S_M^A = C_M^A Q_A \tag{I}$$

where S_M^A is the line recorder peak height or signal at mass M due to gas A. Q_A is the rate of inflow of gas A into the tube and C_M^A is an empirically determined constant.

C_M^A may be considered as the sensitivity of the line recorder to gas A for producing a peak of mass M. As such, its units are

$$\text{output units/c.c. mm./second}$$

if gas flow is measured in cc. mm. per second.

If three gases, A, B, and C enter the tube simultaneously, each producing a signal at mass M, then the total peak height is the sum of the peak heights from each of the three gases, that is

$$S_M = S_M^A + S_M^B + S_M^C = C_M^A Q_A + C_M^B Q_B + C_M^C Q_C \qquad (2)$$

Similar equations will hold for other masses.

The composition of a sample is given by

$$X_A = \frac{Q_A}{Q_A + Q_B + Q_C} \; ; \; X_B = \frac{Q_B}{Q_A + Q_B + Q_C} \; ; \; X_C = \frac{Q_C}{Q_A + Q_B + Q_C} \qquad (3)$$

where the X's are the mol fractions of gases A, B, and C entering the tube. That is, the mol fraction of gas A entering the tube is given by the ratio of the flow of gas A to the total flow into the tube. Therefore, in order to determine the composition of a gas entering the machine from the peak heights recorded by the line recorder, it is necessary to determine the flows by solving equations like (2) and substituting in (3). The calibration of the machine is accomplished by putting known gases in and determining the sensitivities from equation (2). It is in this manner that petroleum and other hydrocarbon analyses may be carried out. Some similar procedure is necessary in analyzing 714, 716, 816, and other fluorocarbon mixtures. A discussion of this problem with numerical results obtained on one line recorder will be given in this section.

In many cases a given mass arises from only one component of the gas stream. In this case, equation (2) becomes identical with equation (1) and is written

$$S_M = C_M Q_A$$

In this case one can solve directly for the various flows without the necessity of solving sets of equations like (2) simultaneously. That is, the flow of a gas is given by the intensity of signal at any peak from that gas divided by the corresponding sensitivity

$$Q_A = \frac{S_M}{C_M} \qquad (4)$$

b. Analysis of Gas Mixtures Containing 616

If some method of measuring total flow, Q_T, is available, then the amount of a given gas present can be determined by measuring the peak corresponding to that gas alone (if no other

gas contributes to the same peak), without the necessity of measuring all other gases present to determine the total flow. Some such scheme is necessary in the line recorder due to the removal of 616 in the chemical trap, which means that the flow of 616 cannot be measured by the spectrometer tube.

Flows are measured in this case by using a Pirani gage to measure the pressure at some fixed point in the system due to the gas flow. It was pointed out in Section I that the pressure at any point in a flow system is given by the product of the gas flow and the resistance to the point of zero pressure, i.e.

$$p = RQ$$

or

$$Q = \frac{p}{R}$$

It is found experimentally that the Pirani reading does not depend only upon the total pressure of gas in it, but can be expressed as a sum of terms arising from the partial pressure of each gas multiplied by a constant which depends upon the gas. That is, one may write for a limited range of variation of the Pirani gage reading, which is symbolized by G,

$$G = g_A \, p_A + g_B \, p_B + g_C \, p_C$$

where p_A is the partial pressure of gas A in the Pirani gage and g_A is a measure of the Pirani gage sensitivity to gas A.

Now the resistance to N_2 differs from that to 616 because, first, the N_2 has zero pressure at the pump whereas 616 has zero pressure at the chemical trap, and second, N_2 has a different molecular weight than 616. Similarly, the 816 has zero pressure at the diffusion pump cold trap and its molecular weight differs from both 616 and N_2. Rewriting the above equation and substituting the product of flow by resistance for pressure, we have

$$G = g_{N_2} R_{N_2} Q_{N_2} + g_{O_2} R_{O_2} Q_{O_2} + g_{816} R_{816} Q_{816} + g_{616} R_{616} Q_{616} \quad (5)$$

which shows that the Pirani reading does not necessarily measure the total flow. This defect may be remedied in a simple manner. Define the corrected Pirani reading K, which shall be used as a measure of the total flow, as

$$K = g_{616} R_{616} Q_T \quad (5a)$$

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From equations (3), (4), and (5a), we have

$$X_A = \frac{S_M}{C_M} \bigg/ \frac{K}{g_{616} R_{616}} \tag{6}$$

Since $\dfrac{C_M}{g_{616} R_{616}}$ is a constant for a given machine, it is con-

venient to symbolize it as a_M.

Thus, equation (6) becomes

$$X_A = \frac{S_M}{K a_M} \tag{6a}$$

It remains to find a relationship between the corrected Pirani reading and the data from the line recorder to enable the calculation of the corrected Pirani reading, K. The total flow is the sum of the flows of all the components

$$Q_T = Q_{N_2} + Q_{O_2} + Q_{616} + Q_{616} \tag{7}$$

Also, equation (4) states

$$Q_A = \frac{S_M}{C_M}$$

which may be written in terms of a_M

$$Q_A = \frac{S_M}{C_M} \frac{g_{616} R_{616}}{g_{616} R_{616}} = \frac{1}{g_{616} R_{616}} \frac{S_M}{a_M} \tag{8}$$

Substituting (5), (7), and (8) into (5a), the value of the corrected Pirani reading is found to be

$$K = g_{616} R_{616} Q_T = G + \left(1 - \frac{g_{N_2} R_{N_2}}{g_{616} R_{616}}\right) \frac{S_{28}}{a_{28}} + \left(1 - \frac{g_{O_2} R_{O_2}}{g_{616} R_{616}} \frac{S_{32}}{a_{32}}\right)$$

$$+ \left(1 - \frac{g_{816} R_{816}}{g_{616} R_{616}}\right) \frac{S_{69}}{a_{69}} \tag{9}$$

where of course one may replace $\dfrac{S_{28}}{a_{28}}$ by its equal $\dfrac{S_{14}}{a_{14}}$ if the 28 peak is off scale. The form of equation (9) leads to the definition of the Pirani gage correction factors

$$A_{N_2} = 1 - \frac{g_{N_2} \; R_{N_2}}{g_{616} \; R_{616}}$$

$$A_{O_2} = 1 - \frac{g_{O_2} \; R_{O_2}}{g_{616} \; R_{616}}$$

$$A_{816} = 1 - \frac{g_{816} \; R_{816}}{g_{616} \; R_{616}}$$

The mol fraction of impurity in the sample is given by the ratio of the signal from that impurity to the product of the corrected Pirani reading with the sensitivity

$$X_{N_2} = \frac{S_{28}}{a_{28} K} = \frac{S_{14}}{a_{14} K}$$

$$X_{O_2} = \frac{S_{32}}{a_{32} K}$$

$$X_{816} = \frac{S_{69}}{a_{69} K} = \frac{S_{131}}{a_{131} K} \tag{10}$$

The corrected Pirani reading for the sample is obtained by adding to the Pirani reading terms consisting of the Pirani correction factor for a gas multiplied by the ratio of peak height to sensitivity for that gas.

$$K = G + A_{N_2}\left(\frac{S_{28}}{a_{28}} \text{ or } \frac{S_{14}}{a_{14}}\right) + A_{O_2}\frac{S_{32}}{a_{32}} + A_{816}\left(\frac{S_{69}}{a_{69}} \text{ or } \frac{S_{131}}{a_{131}}\right) \tag{11}$$

The definition of the symbols in equations (10) and (11) are summarized here.

X_A ≡ mol fraction of gas A in sample

a_M ≡ sensitivity of spectrometer for mass M

A_M ≡ Pirani gage correction factor for gas A

S_M ≡ peak height for mass M as measured by line recorder for the sample.

G ≡ Pirani gage reading

K ≡ corrected Pirani gage reading

An example of calculations for unknown samples is given in Section II.3-e.

Although equations (10) and (11) have theoretical signifi-cance due to the manner of their derivation, in actual use of the line recorder, equations (10) and (11) are taken as the fundamental equations which are justified empirically. It is to be noted that additional gases may be considered by adding corresponding terms to (10) and (11).

From the definitions of A_{N_2} and A_{O_2} it seems likely they will be equal. This has been confirmed experimentally. A sample consisting of 100% air is admitted to the line recorder and data taken. This is followed by 100% N_2. The data follow:

% O_2	% N_2	Pirani	S_{14}
0	100	50.0	4450
21	78	50.2	3480

For the first sample, from equation (10).

$$\frac{K}{G} \equiv \frac{S_{14}}{G \cdot X_{N_2} a_{14}} = \frac{89}{a_{14}}$$

For the second sample

$$\frac{K}{G} \approx \frac{89}{a_{14}}$$

Hence $\frac{K}{G}$ first sample ≡ $\frac{K}{G}$ second sample

But, from equation (11)

$$1 = \frac{G}{K} + A_{N_2} \frac{S_{14}}{a_{14}K} + A_{O_2} \frac{S_{32}}{a_{32}K} + A_{C816} \frac{S_{69}}{a_{69}K}$$

or using (10)

$$\frac{G}{K} = 1 - A_{N_2} X_{N_2} - A_{O_2} X_{O_2} - A_{816} X_{816} \qquad (12)$$

For first sample

$$\frac{G}{K} = 1 - A_{N_2}$$

For second sample

$$\frac{G}{K} = 1 - 0.78 A_{N_2} - 0.21 A_{O_2}$$

Since these are equal, we have

$$A_{N_2} = A_{O_2}$$

to sufficient accuracy. Hence, the Pirani correction factor is the same for oxygen as for nitrogen. We call this A_{air}. It remains to be shown directly that equations (10) and (11) hold for the line recorder. To do this, we note that

$$\frac{G}{K} = \frac{G \, a_{14} \, X_{N_2}}{S_{14}} \qquad \text{from (10)}$$

$$= 1 - A_{N_2} X_{N_2} - A_{816} X_{816} \qquad (12a)$$

from (12) if we use mixtures containing 816, N_2, and 616 only. Equation (12a) indicates that if $\frac{G X_{N_2}}{S_{14}}$ is plotted against X_{N_2}

for constant X_{816} and varying amounts of N_2 and 616, we should obtain a straight line. Further, if the process is repeated for another 816 concentration a parallel line should be obtained. The results of such a test are given in Figure II.3-1. That both lines are straight is evident. **Data are available to support** this for 0% 816 in addition to that plotted here.

However, the lines do not appear to be parallel. If the
dotted line is drawn as shown through one end of the 5% 816 curve
parallel to the 0% 816 curve it differs from the 5% 816 curve
at the other end by 7%. However, this is an extreme case; for less
air or less 816 the agreement will be much closer. One may con-
clude that equations (12a) and therefore (10) and (11) are valid
as an approximation which will be excellent if the 816 concentra-
tion does not vary very much or if calibration data are obtained
with the plant concentration of 816.

The principal symbols used in this section with their
definitions and units are tabulated for reference.

Symbol	Definition	Units
S_M	Intensity of peak at mass M as measured on the line recorder.	The basic unit of measuring intensities is 2 mv. This unit is called an "Intensity Unit."
G	Pirani reading	Same as for S_M.
K	Pirani reading corrected to give a true measure of total gas flow into tube.	Same as for S_M.
X_A	Mol fraction of gas A in sample	Numeric.
a_M^A	Sensitivity of spectrome- ter to gas A in measuring a peak at mass M.	Peak intensity per unit corrected Pirani reading per unit concentration of gas A in sample.
a_M	Brief notation for a_M^A when the peak at mass M is produced only by gas A of all the gases in the sample.	Same as for a_M^A.
A_A	Pirani gage correction factor for gas A.	Change in Pirani reading per unit peak intensity per unit sensitivity.

For mixtures containing N_2, O_2, 816, and 616 only:

$$X_{N_2} = \frac{S_{14}}{a_{14}K} = \frac{S_{28}}{a_{28}K} \quad ; \quad X_{O_2} = \frac{S_{32}}{a_{32}K} \quad ; \quad X_{316} = \frac{S_{69}}{a_{69}K} = \frac{S_{131}}{a_{131}K}$$

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$$K = G + A_{air}\left(\frac{S_{14}}{a_{14}} \text{ or } \frac{S_{28}}{a_{28}} + \frac{S_{32}}{a_{32}}\right) + A_{816}\left(\frac{S_{69}}{a_{69}} \text{ or } \frac{S_{131}}{a_{131}}\right)$$

c. Analysis of 616 Containing Small Amounts of Impurities

When the amount of impurity in 616 becomes small, the connection terms for the Pirani gage become insignificantly small. Equation (11) then reduces to

$$K = G$$

Equation (10) becomes

$$X_{N_2} = \frac{S_{28}}{a_{28}\,G} = \frac{S_{14}}{a_{14}\,G}$$

$$X_{O_2} = \frac{S_{32}}{a_{32}\,G}$$

$$X_{816} = \frac{S_{69}}{a_{69}\,G}$$

The following table gives typical signals for 1% impurities of various gases and the corresponding Pirani gage corrections. The Pirani gage is set at 50 in each case.

Gas	Peak	Pirani Gage Correction Factor	Sensitivity	For One Per Cent Impurity	
				Signal	Pirani Gage Correction
816	69	-6.9	3300	1550	-3.2
SiF_4	85	0.84	882	445	0.4
CO_2	44	-0.65	767	386	-0.3
N_2O	30	0.93	149	75	0.5
714	69	-5.3	2740	1370	-2.6
BF_3	49	-1.4	103	50.8	-0.7
HF	20	-0.4	320	160	-0.2
N_2	14	-0.03	56	28	-0.01

d. Determination of Calibration Constants

In order to determine the sensitivities and Pirani gage correction factors for the line recorder, a sufficient number of calibration samples must be used. Equation (10) may be written:

$$K = \frac{S_{14}}{a_{14} X_{N_2}} = \frac{S_{28}}{a_{28} X_{N_2}} = \frac{S_{32}}{a_{32} X_{O_2}} = \frac{S_{69}}{a_{69} X_{816}} \qquad (13)$$

which shows that the ratio of the sensitivities can be determined from the data on any one sample containing 816, N_2, and O_2. It is necessary to have sufficient additional information to determine the absolute value of one sensitivity and the values of the Pirani gage correction factors. To do this it is advisable to write (10) and (11) in a form suitable for calibration. This form is:

$$\frac{S_{14}}{G \, X_{N_2}} = a_{14} + a_{14} A_{air} \frac{S_{14}}{G \, a_{14}} + \frac{S_{32}}{G \, a_{32}} + A_{816} \frac{S_{69}}{G \, a_{69}} \, a_{14}$$

Now, for air, from (13)

$$\frac{S_{32}}{a_{32}} = \frac{X_{O_2}}{X_{N_2}} \frac{S_{14}}{a_{14}}$$

$$\frac{S_{14}}{a_{14}} + \frac{S_{32}}{a_{32}} = \frac{X_{O_2} + X_{N_2}}{X_{N_2}} \frac{S_{14}}{a_{14}} = \frac{1}{0.78} \frac{S_{14}}{a_{14}} = 1.28 \frac{S_{14}}{a_{14}}$$

Also, for any sample

$$\frac{S_{69}}{a_{69}} = \frac{X_{816}}{X_{N_2}} \frac{S_{14}}{a_{14}}$$

Hence,

$$\frac{S_{14}}{G \, X_{N_2}} = a_{14} + 1.28 A_{air} \frac{S_{14}}{G} + A_{816} \frac{X_{816}}{X_{N_2}} \frac{S_{14}}{G}$$

Or, noting that $X_{air} = 1.28 X_{N_2}$

$$\frac{S_{14}}{G X_{air}} = \frac{a_{14}}{1.28} + A_{air}\frac{S_{14}}{G} + \frac{X_{816}}{X_{air}} A_{816}\frac{S_{14}}{G} \tag{14}$$

Equation (14) contains three unknowns, a_{14}, A_{air}, and A_{816} and therefore requires three calibration samples for its solution. Using these, three methods suggest themselves for evaluating (14):

1. Substitute the data for each of the three samples in (14) in turn and solve the resulting relations simultaneously.

2. Solve for the constants by the graphical procedure given below.

3. Solve the simultaneous equations of method one for the constants before substituting the calibration data.

The graphical method of solution is carried out in Figure II.3-2 for the following typical calibration data.

CALIBRATION DATA

Sample	% Air	% 816	Pirani	S_{14}	S_{28}	S_{32}	S_{69}
1	10	0	50.2	333	4700	996	---
2	100	0	50.0	4250	off scale	off scale	---
3	10	2	50.0	296	4200	876	4740

One first calculates

Sample	$\dfrac{S_{14}}{G}$	$\dfrac{S_{14}}{X_{air} G}$
1	6.63	66.3
2	85.0	85.0
3	5.92	59.2

These three points are plotted on a graph of $\dfrac{S_{14}}{X_{air}}$ vs. $\dfrac{S_{14}}{G}$ (Figure II.3-2). The slope of this line gives A_{air} and the $\dfrac{S_{14}}{X_{air} G}$ axis intercept gives $a_{14}/1.28$. A second line is drawn connecting the point for sample 3 with the intercept of the first line and the vertical axis. The slope of this second line is $A_{air} + \dfrac{A816 \, X_{816}}{X_{air}}$.

From the construction of Figure II.3-2, we have

$$a_{14} = 33.2$$

$$A_{air} = 0.24$$

$$A_{816} = 6.1$$

Equation (13) is used to find the remainder of the sensitivities.

$$a_{28} = \frac{S_{28}}{S_{14}} \, a_{14} = \frac{4700}{333} \times 83.2 = 1170$$

$$a_{32} = \frac{X_{N_2}}{X_{O_2}} \frac{S_{32}}{S_{14}} \, a_{14} = \frac{0.78}{0.21} \frac{996}{333} \times 83.2 = 920$$

$$a_{69} = \frac{X_{N_2}}{X_{816}} \frac{S_{69}}{S_{14}} \, a_{14} = \frac{0.078}{0.020} \times \frac{4740}{296} \times 83.2 = 5170$$

Method three actually consists of doing the above process analytically. We indicate data from sample one by enclosing it in $(\ )_1$ and similarly for samples two and three.

$$a_{14} = 1.28 \frac{\frac{1}{(X_{air})_1} - \frac{1}{(X_{air})_2}}{\left(\frac{G}{S_{14}}\right)_1 - \left(\frac{G}{S_{14}}\right)_2}$$

$$= 1.28 \frac{\frac{1}{0.100} - \frac{1}{1.00}}{\frac{50.2}{333} - \frac{50.0}{4250}} = 83.2$$

$$A_{air} = \frac{\left(\frac{S_{14}}{X_{air}G}\right)_2 - \left(\frac{S_{14}}{X_{air}G}\right)_1}{\left(\frac{S_{14}}{G}\right)_2 - \left(\frac{S_{14}}{G}\right)_1} = \frac{85 - 66.3}{85 - 6.63} = 0.24$$

$$A_{816} = \left(\frac{X_{air}}{X_{816}}\right)_3 \left\{ A_{air} + \frac{\frac{a_{14}}{1.28} - \left(\frac{S_{14}}{X_{air}G}\right)_3}{\left(\frac{S_{14}}{G}\right)_3} \right\}$$

$$= -5 \left(0.24 + \frac{65.0 - 59.2}{5.92} \right) = -6.1$$

The remainder of the sensitivities are calculated as before. Tabulating the results:

$$a_{14} = 83.2$$

$$a_{28} = 1170$$

$$a_{32} = 920$$

$$a_{69} = 5170$$

$$A_{air} = 0.24$$

$$A_{816} = -6.1$$

Hence, the line recorder calibration is completely known. An example of the evaluation of unknown samples follows:

e. Analysis of Unknown Samples

The data for the unknowns are:

DATA ON UNKNOWNS

Sample	Pirani	S_{14}	S_{28}	S_{32}	S_{69}
a	51	32	453	45	2100

(cond't)

SAMPLE	Pirani	S_{14}	S_{28}	S_{32}	S_{69}
b	50.7	386	5450	600	150
c	50.0	3250	Off Scale	3000	1000
d	49.5	3	36	2	5000

In actual calculations of the samples one needs first of all the signals divided by their sensitivities. That is, one needs to calculate the following table:

TABLE IV

Sample	$\dfrac{S_{14}}{83.2}$	$\dfrac{S_{28}}{1170}$	$\dfrac{S_{32}}{920}$	$\dfrac{S_{69}}{5170}$
a	0.385	0.386	0.049	0.406
b	4.64	4.64	0.653	0.0290
c	39.1	-----	3.26	0.193
d	0.036	0.031	0.002	0.965

The next step is to calculate the corrected Pirani gage readings using equation (13).

$$K = G + 0.24 \left(\frac{S_{14}}{83.2} \text{ or } \frac{S_{28}}{1170} + \frac{S_{32}}{920} \right) - 6.1 \frac{S_{69}}{5170}$$

TABLE V

Sample	G	$0.24 \dfrac{S_{14}}{83.2}$	$0.24 \dfrac{S_{28}}{1170}$	$0.24 \dfrac{S_{32}}{920}$	$6.1 \dfrac{S_{69}}{5170}$	K
a	51		0.1	0	2.5	48.6
b	50.7		1.1	0.2	0.2	51.8
c	50.0	9.4		0.8	1.2	59.0
d	49.5		0	0	5.9	43.6

We then divide the values of the peak heights over sensitivities in Table IV by the K's of Table V to yield the sample compositions. All values have been multiplied by 100 to give the results in per cent.

TABLE VI

Sample	% N_2	% O_2	% C-816
a	0.79	0.10	0.83
b	8.95	1.26	0.056
c	66.5	5.55	0.328
d	0.071	0.005	2.21

It should be noted that $\frac{S_{14}}{X_{14}}$ and $\frac{S_{28}}{X_{28}}$ both measure the per cent nitrogen and should therefore be equal. For small amounts of nitrogen the mass 28 peak may be expected to be more reliable than the mass 14 peak, since it is the larger. Therefore, when the mass 28 peak is on scale, it is used. When it is not on scale the mass 14 peak is used in its place. Similarly, when the 69 peak goes off scale for 816, the 131 peak is used in its place.

f. Detection of Fluorocarbon Traces in 616

One of the applications to which the line recorder has been put is detecting traces of fluorocarbons in 616. In order to test a representative sample, the 616 is liquified and a small amount of liquid removed and allowed to expand until completely vaporized. With the manifold shown in Figure II.1-20, a sample of approximately 200 milligrams is required although analyses could be made with much less material if a special manifold with low volumes were employed.

To make an exact analysis is impossible without a calibration of the instrument with all of the fluorocarbons which are expected. However, since usually it is necessary only to determine the fluorocarbon content approximately, certain simplifications are possible. The mass 69 peak (CF_3) is used for this work. It has been found that the intensity of this peak is approximately the same for all fluorocarbons so far investigated. Shown below are the sensitivity factors for the 131, 69, and 31 peaks for several fluorocarbons.

	Mol. Wt.	a_{69}	a_{131}	a_{31}
816	400	3100	202	314
716	388	3900	330	320
methyl cyclohexane	350	2640	297	647
dimethyl cyclopetane	350	1550*		
ethyl cyclopetane	350	1240*		

        * These values were determined earlier with a different instrument and are shown here relative to the three others for comparison. a_{131} and a_{31} were not determined at that time.

    Since the sensitivity of a line recorder depends upon the operating conditions and will vary from one machine to another, and from one time to another, the instrument should be calibrated at the time unknowns are analyzed. For this purpose a test sample containing between 1/2 and 1 mol per cent of 816 in 616 is used. The a_{69} is determined in the manner discussed in Section II.3-d. Let us assume a_{69} is found to be 3100 as given in the above table.

    Now let us assume that an unknown sample is analyzed for which it is found that the Pirani gage flowmeter read 50 units and that the positive ion current corresponding to the 69 peak was 155 units. Then if we assume the unknown sample contains only 816 as an impurity the mol fraction will be:

$$X_A = \frac{S_{69}}{a_{69} \, G} = \frac{155}{3100 \times 50} = 0.001 \text{ or } 0.1\%$$

If, on the other hand, one assumes that the impurity consisted of equal parts of the five components listed above, the sensitivity factor to use would be the average of the five given, or 2490. The X_A calculated would then be 25% higher. In any event it is seen that since the a_{69}'s for the fluorocarbons, which we know about, are of the same order of magnitude, no serious error is made whatever assumption is made. In making the above calculation we assumed that the sample analyzed was essentially free of components other than fluorocarbons and 616. If this is not the case the more accurate expression K for the corrected Pirani gauge reading will have to be used in place of G.

It is recommended that until such time that data to the contrary are available it be arbitrarily assumed that the answer obtained using the 816 calibration should be multiplied by 1.25. Accordingly in the sample discussed above the final X_A would be given as 0.125%. Since in all work on the line recorder mol fractions and percentages are used, it will be necessary to use suitable conversion factors if weight per cent's are desired.

The analysis of small amounts of fluorocarbon in 616 is complicated by the residual readings on the line recorder. A residual signal of

$$S_{69} = 10$$

corresponds to

$$\% \ 816 = 100 \ \frac{S_{69}}{a_{69} \ G} = \frac{1000}{3100 \times 50} = 0.006\%$$

With care and patience the S_{69} residual can be brought as low as 2, which then corresponds to .001% C-816. With percentages as low as these, it is necessary to use the output meter rather than the recorder. In this case, 0.001% 816 corresponds (on the most sensitive shunt) to 40 out of 200 full scale on the meter. But it is uncertain how reliable readings are when the residual is of the order of magnitude of the per cent being measured. It would seem that the lower limit of 816 determinations in 616 would then be near 0.001% 816.

g. Detection of 714 in the Presence of 816

In order for the line recorder to differentiate 714 from 816, the ratio of two different peak heights must differ from that of 816. But we have seen that such is the case:

	a_{69}	a_{131}	a_{69}/a_{131}
816	3100	314	9.9
714	2640	647	4.1

(on any given line recorder, these values are checked periodically if they are needed.)

If it be assumed that neither the 131 nor the 69 peaks arise from any other gases present in the sample than 714 and 816, one may write

$$S_{69} = K \left(a_{69}^{316} X_{816} + a_{69}^{714} X_{714} \right)$$

$$S_{131} = K \left(a_{131}^{816} X_{816} + a_{131}^{714} X_{714} \right)$$

Solving simultaneously, one obtains

$$\text{mol fraction 714 in 816} = \frac{X_{714}}{X_{714} + X_{816}} = \frac{a_{69}^{816} - a_{131}^{816} \dfrac{S_{69}}{S_{131}}}{\left(a_{131}^{714} - a_{131}^{816} \right) \dfrac{S_{69}}{S_{131}} + a_{69}^{816} - a_{69}^{714}}$$

For the numerical values quoted above, this becomes

$$\text{Mol fraction 714 in 816} = \frac{3100 - 314 \dfrac{S_{69}}{S_{131}}}{460 + 333 \dfrac{S_{69}}{S_{131}}}$$

It may be noted that a two per cent change in $\dfrac{S_{69}}{S_{131}}$ is approximately the minimum measureable with the line recorder. This corresponds to 1.6 mol per cent 714 in the 816.
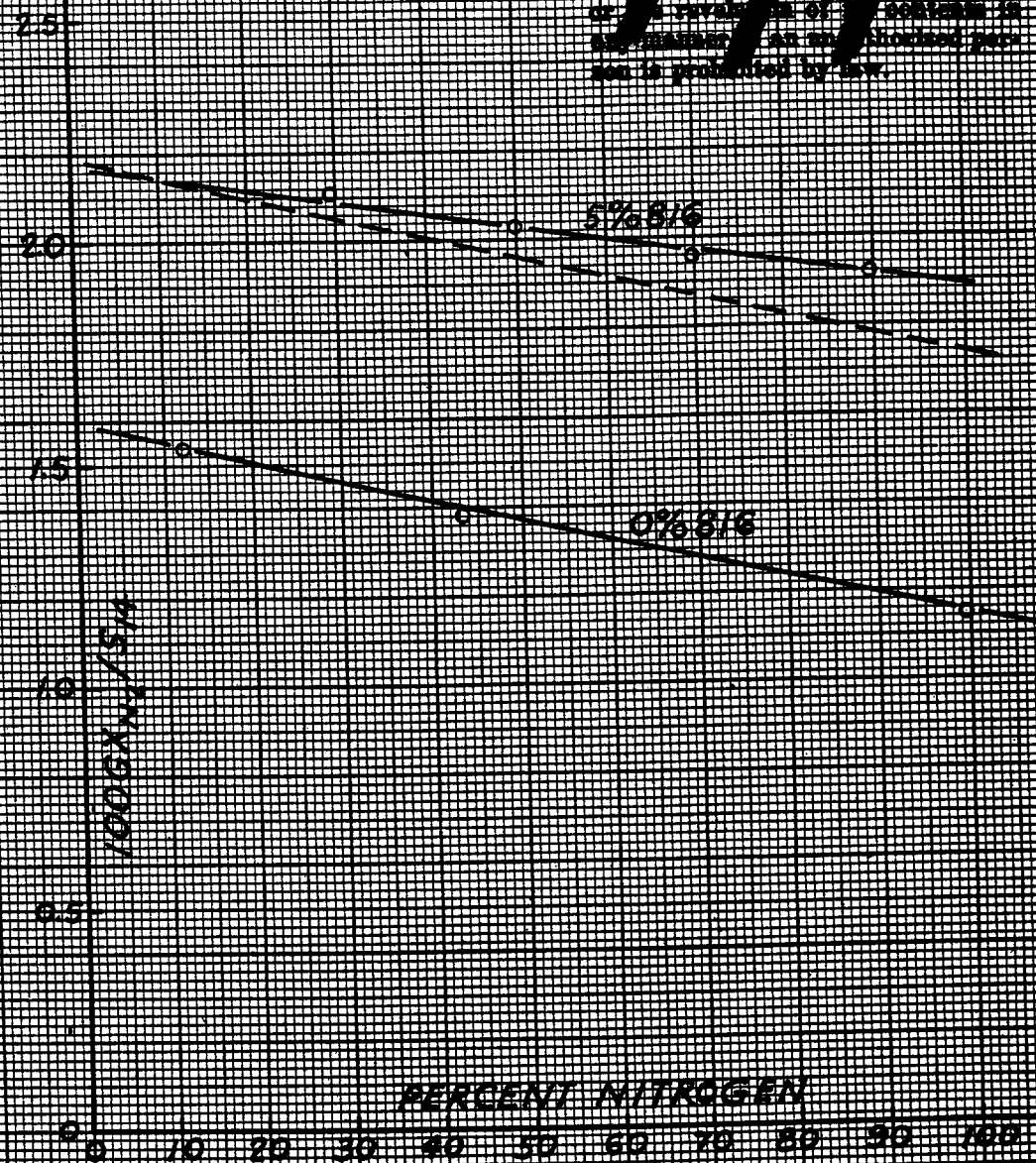
CALIBRATION CURVES
FOR A LINE RECORDER

FIGURE II.3-1

SAMPLE 2

SAMPLE 1

SAMPLE 3

$SLOPE = A_{AIR} = 0.24$

$INTERCEPT = C_{14} = 65.0 \qquad C_{14} = 83.2$

$SLOPE = A_{AIR} + (X_{B16} / X_{AIR}) A_{B16} = -0.98$

$A_{B16} = -\dfrac{0.100}{0.0200} (0.98 + 0.24) = -6.1$

S_{14}/G

$S_{14}/(C_{14}\,G)$
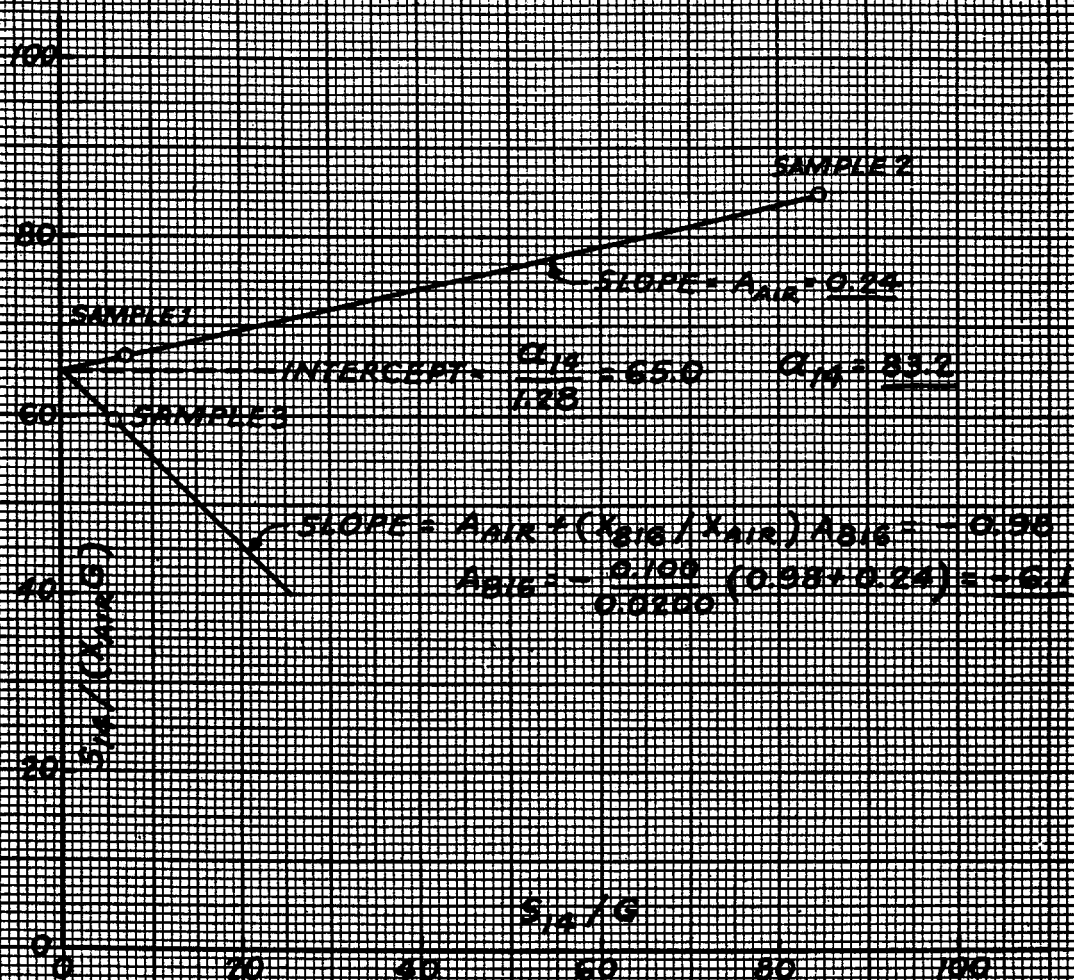
GRAPHICAL DETERMINATION
OF CALIBRATION CONSTANTS
FOR A LINE RECORDER

FIGURE II3-2

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4. Characteristics And Design of Line Recorder

a. General Requirements

Previous sections have dealt with the function and operation of the line recorder. Of primary concern in this section will be the design and characteristics of the line recorder and the factors influencing them. Representative data will be supplied wherever possible to supplement description. In many cases lack of time has not permitted the exploitation of design alternatives.

To reiterate briefly, the line recorder is an instrument enabling a continuous quantitive analysis of gaseous mixtures. The fundamental measurements made are those of flow, mass, and ion currents. Let us consider the overall requirements to be met by the combined components of an operable line recorder and then investigate the implications of these requirements in view of physical achievement and practical design.

(1) Accurate means of measuring mass, flow, and ion currents must be provided.

(2) The analyzed gas composition should be a single valued function of the measured quantities or combination thereof.

(3) The measurements must be independent of uncontrolled variables and relatively independent of variables whose control is limited for practical reasons.

In addition to these requirements, consideration must be given to other factors, such as ease of operation, maintenance, and simplicity. The functional relations involved in calculating the answers should be simple and direct.

b. Measurement of Mass

The method of measuring mass has been discussed in Section I-5 and Section II-1. Accurate measurements require constancy of magnetic and electric fields plus ability to separate mass. By using a permanent alnico magnet constant magnetic field has been obtained. Adequately regulated electronic voltage supplies insure constant electric fields. The geometry of the line recorder tube has been so designed that adequate mass separation is obtained for its proposed use. It is essential that the magnetic and electric fields employed be properly adjusted and aligned. Further discussion on this point will be included later.

c. Measurement of Ion Currents

Measurement of ion currents is made with a feedback amplifier as discussed in Section II-1. With its electronically stabilized power supplies and other stabilizing features, it presents no limitation on the accuracy of present line recorders. Only in measuring extremely small quantities of impurities does its zero shift or noise level cause any difficulty. Adequate shielding of its high impedance imput circuit is insured by the all metal construction of the collector and preamplifier housing.

d. Measurement of Flow

The measurement of flow centers around the Pirani Gauge. In Section I-1 there were discussed the principles involved and the manner in which flow is calculated. It is evident that the measurement is no simple matter and that several factors are involved. Obviously, the power supplied to the gauge must be constant. An electronically controlled voltage source solves the problem of constant supply. Experimentally it is found that an increase of two per cent in Pirani bridge current at operating pressure will decrease the Pirani readings by about five per cent. The gage elements themselves must be reliable and not subject to deterioration or change of characteristics. The corrosive nature of the gases involved limit the choice of elements for construction. Constructional difficulties further restrict the choice. Nickel was finally chosen for the gage element. When properly constructed and handled, nickel gages were found to be very reliable and showed little or no zero drift or change in sensitivity over long periods of time.

Figure II.4-1 which depicts the overall performance of a line recorder, is evidence to the performance of a Pirani gage over extended periods of time. Samples were prepared from day to day to obtain the line recorder readings, which are shown plotted as a function of time. Irregularities represent changes from all components of the line recorder and include any errors in sample mixing.

It should be emphasized that care must be exercised in keeping the gage and element clean. Soldering should be done in a deoxidizing atmosphere. Failure to observe these precautions may result in a gage which drifts and reaches equilibrium only after a long period of operation. Operation of the gage with atmospheric air also results in instability for a considerable time afterwards.

For purposes of support and ruggedness the Pirani gage element was made from 3 mil nickel wire. The resulting mass has appreciable thermal capacity, which gives rise to a time lag in reaching thermal equilibrium.

Figure II.4-2 depicts the Pirani gage reading and mass 28 peak as a function of time. It shows the effect of an abrupt change in pressure behind the leak upon both of these readings. Note that the mass 28 peak reaches its final value almost immediately, while the Pirani gage takes from three to six minutes, depending upon the magnitude of the pressure change.

Several other elements were suggested which might enable practical construction and permit lower thermal capacity. Several alloys of platinum were tried with some success. Due to lack of time, however, the possibilities were not fully exploited. Tungsten was found to be insufficiently inert from a chemical standpoint.

The resistance of the gage element depends upon ambient temperature. Proper design, however, permits automatic correction for this variable at a given pressure in a simple manner. By placing another nickel element of proper resistance in the same block as the gage element so that it experiences the same ambient temperature it can, as a portion of one bridge arm, be made to compensate for the gage element. The remainder of the bridge arms are made of manganin, which displays little temperature coefficient. The compensation is made exact at an appropriate pressure. At other pressures over compensation or under compensation occurs. By limiting the operating pressure range errors due to ambient temperature can be made negligible.

Figure II.4-3 shows the actual variation in gage reading with ambient temperature. In examining this figure and other experimental data presented in this report, it is well to bear in mind that the data were taken on different line recorders at various times and will therefore not be self consistent. The gage used in this experiment was a standard gage except that 10 ohms compensating resistance is used rather than 8. Without compensation one would expect the reading to decrease as temperature increases. The compensating resistance, however, has reversed the effect for the two cases shown in Figure II.4-3. By going to higher pressures it would be found that the curves would level off and finally begin sloping the other way. Note that at zero pressure the Pirani gage reading is very much dependent on ambient temperature. This fact should be born in mind when any zero adjustment is contemplated.

Another factor which must be considered in using the Pirani gage is the relation between gage reading and pressure. Whereas the relation is almost that of straight proportionality at low pressure, it deviates to some extent at higher pressures. Figure II.4-4 gives an actual static calibration curve for a

Pirani gage with nitrogen. Pressure measurements were made with a double sylphon pressure gage. Figure II.4-5 was obtained from a line recorder by plotting the mass 14 peak against Pirani reading while varying the amount of air flowing into the line recorder. Linearity would permit operation over wide pressure ranges with little or no complication in the calculation of the analysis. However, for accuracy considerations the range should be as limited as possible consistent with ease of adjusting the leak.

Since the Pirani gage is basically a pressure measuring device, the resistance, which relates pressure to flow, figures importantly in the measurement. The principles involved in the flow of gases at low densities are discussed in Section I-2. Section II-3 also discusses the subject of resistance to flow and how it enters into the calibration of the line recorder. It is evident that the entire gas flow system must be carefully designed if accurate flow measurements are to be taken. Constancy of resistance to flow is of prime importance. In general, for a given configuration, the resistance is a function primarily of geometry and is proportional to the square root of the ratio of mass to absolute temperature. Any action whereby a molecule is removed or added to the flowing gas constitutes a pumping action or its reverse and must be properly accounted for.

The major portion of the resistance to flow is due to the nickel tubing inserted in the flow lines. This assures constant geometry. Being relatively inert to the gases expected to be encountered, nickel tubing may be expected to be relatively free of errors due to selective removal of gas passing through the tubing. Care must be exercised as to cleanliness of the tubing. Any foreign matter is very apt to add or remove gas from that flowing through to be analyzed.

Since the pumping speed of the tubing varies only as the square root of the absolute temperature, temperature changes are not critical. A change in ambient temperature from 20°C to 30°C changes the resistance by 1-1/2 per cent.

With the exception of 616, which is removed by the chemical trap, gases are removed either by condensation in the cold trap or are pumped out through the diffusion pump. In certain cases there may be some removal by reaction with the hot tungsten filament or with other material. These removal elements involve a certain amount of pressure drop and consequently have an effective resistance. Any variation in these effective resistances will have a bearing on the resistance to flow. Fortunately in the case of the cold trap and the diffusion

pump, the effective resistances involved are small in comparison to the total resistance to flow at the Pirani gage. For example, the resistance to air at the Pirani gage is around 360 sec/liter while the effective resistance of the pump involved is of the order of 0.1 sec/liter. Evidently the pump effective resistance can vary by an appreciable factor without influencing the measurement of flow. As will be seen later, however, these effective resistances are more important from another standpoint.

The chemical trap used to remove 616 presents a much more difficult problem in keeping the resistance to 616 at the Pirani gage constant. Actually, the resistance depends upon total flow and composition of the gas due to shift in reaction point. The maintenance of a nearly constant flow and the fact that the variation of resistance is such that it merely changes the value of the constants of Section II-3 has permitted successful use of the chemical trap. The design will be considered in more detail later on.

It was pointed out in Section II-3 that all gases do not give the same response on a Pirani gage. The corrected Pirani gage reading as defined in Section II-3 is designed to account for these differences.

e. Design of Gas Inlet Lines & Chemical Trap

In designing the chemical trap and gas inlet several requirements as to magnitude and practicability must be considered.

1. The Pirani gage should register about (100 mv) under normal operating conditions with the 616 consumption at the rate of 40 mg/day.

2. Since air or nitrogen will probably be of most interest, the sensitivity to air or nitrogen should be independent of its concentration.

3. The chemical trap should be relatively independent of variables such as temperature and should be reliable over a long period of time with a minimum of attention.

A consumption of 40 mg/day of 616 at 25°C is equivalent to a flow of 2.44×10^{-2} cc mm/sec. This requires a definite resistance at the Pirani gage to obtain a 100 mv signal. Experimental data show the following relations to be reasonably accurate. For pure 616:

$$\text{Pirani in mv} = 1.8 \times 10^4 \, P_{616} \qquad (1)$$

For pure air:

$$\text{Pirani in mv} = 1.15 \times 10^4 \, P_{air} \tag{2}$$

Pressures are measured in mm of Hg. Replacing the pressure by its equivalent, the product of flow and resistance.

$$\text{Pirani} = 1.8 \times 10^4 \, R_{616} \, Q_{616} \tag{3}$$

$$\text{Pirani} = 1.15 \times 10^4 \, R_{air} \, Q_{air} \tag{4}$$

Since we desire a 100 mv signal with a flow of 616 equal to 2.44 $\times 10^{-2}$ cc mm/sec. R_{616} is from (3)

$$R_{616} = \frac{100}{1.8 \times 10^4 \times 2.44 \times 10^{-2}} = \underset{0.227}{\cancel{0.232}} \text{ sec/cc.}$$

The resistance to 616 of 1/4" nickel tubing is on the average about 7.4 $\times 10^{-3}$ sec/cc/in. This resistance is based on tubing with 0.173" inside diameter. The inside diameter of tubing may vary from batch to batch. Hence the length of 1/4" nickel tubing required would be

$$L = \frac{\underset{22.7}{\cancel{232}} \times 10^{-3}}{7.4 \times 10^{-3}} = \underset{30.7}{\cancel{31.4}} \text{ inches}$$

It is an observed fact that the air signal on the line recorder is proportional to the flow of air. This means that, if the sensitivity to air (air signal/Pirani) is to be independent of air concentration, the Pirani gage should register 50 with a flow of 2.44 $\times 10^{-2}$ cc mm/sec of pure air. From (4) we calculate R_{air}:

$$R_{air} = \frac{100}{1.15 \times 10^4 \times 2.44 \times 10^{-2}} = 0.356 \text{ sec/cc.}$$

For air, the resistance of 1/4 in. nickel tubing is on the average 2.1 $\times 10^{-3}$ sec/cc in. If the resistance to air is provided entirely by 1/4 in. nickel tubing, the length required is:

$$L = \frac{356 \times 10^{-3}}{2.1 \times 10^{-3}} = 170 \text{ inches}$$

A suitable gas inlet system might be constructed as shown in Figure II.4-6. The Pirani is connected to the inlet side of 170" of 1/4" nickel tubing. 31.4" from the Pirani gage a 616 remover is attached. We assume that the 616 pressure is zero at the 616 remover while all other gases fall to zero pressure at the

gas remover. In actual practice the resistance provided by the 170" of 1/4" nickel tubing shown in Figure II.4-6 is made up of a series of elements including effective resistances of diffusion pump and cold trap, resistance of Line Recorder tube, 1/8" nickel tubing 1/4" nickel tubing, valves, etc. The resistance from the source to the pump amounts to the equivalent of two or three inches of 1/4" nickel tubing. The 616 is removed by chemical reaction with mercury. A pool of mercury is inserted at the proper place between the Pirani gage and line recorder tube. Figure II.4-7 shows the mechanical layout of the chemical trap. The cold spot is used to confine the reaction region and to limit the mercury pressure. The supposed action is as follows:

Mercury distills from the mercury reservoir and diffuses through the 1/8" holes up the nickel tube and upon reaching the cold spot condenses in sufficient quantities to reduce the pressure of mercury at this point to its usual value at the temperature of the cold spot. The uncondensed mercury then continues on and reacts completely with the 616 a short distance up the tube.

Excessive quantities of distilled mercury may drop back into the reservoir together with any reaction products which flake off the walls of the tube. To prevent these reaction products from "poisoning" the mercury surface, the nickel tubing is extended below the surface so that the region below the 1/8" holes acts as a trap.

It is essential for proper operation that the flow of mercury from the reservoir to the cold spot equal or exceed the flow of 616. A factor of two is recommended to take care of temporary high 616 flows. This requirement limits the distance from the cold spot to the mercury reservoir for a given tubing size. In Figure II.4-8 this distance is shown as 6" of 1/4" nickel tubing. If we assume the mercury pool at room temperature (25°C) and the cold spot at -20°C, the flow will be approximately,

$$\frac{P_{Hg\ 25°C} - P_{Hg-20°C}}{R_{Hg}} = \frac{1.8 \times 10^{-3}}{13.1 \times 10^{-3} \times 2.64} = 5.2 \times 10^{-2}\ cc.\ mm/sec.$$

To make certain that the Hg does not condense before reaching the cold spot, a warming fin is attached. This also prevents any excessive cooling of the reservoir and thus assures ample flow of mercury to the cold spot. Should the condensation point shift, the point of reaction with 616 would also tend to shift. This would be equivalent to changing the position of the 616 remover shown in Figure II.4-6 and hence would alter the Pirani gage reading.

The location of the reaction point depends upon the temperature of the cold spot. The nature of the dependence can be predicted by calculating the position of the actual point of reaction. Since one mole of 616 reacts with one mole of mercury the flow of mercury must equal the flow of 616 at the reaction point. Assume that a mercury supply exists at the cold spot and furthermore that the pressure of mercury at the cold spot, P_{Hg}, is determined by the temperature of the cold spot. Knowing the flow of mercury, the resistance to the point of zero pressure of mercury, which is the reaction point, can be determined. Hence we may write

$$\frac{P_{Hg}}{R_{Hg}} = Q_{616}$$

where R_{Hg} is the resistance to flow of mercury measured from cold spot to reaction point. Solving for R_{Hg} and substituting the normal value of Q_{616}

$$R_{Hg} = \frac{P_{Hg}}{2.44 \times 10^{-2}}$$

For 1/4" nickel tubing the resistance to flow for mercury is about 5.5 $\times 10^{-3}$ sec/cc in. Hence, if 1/4" nickel tubing is used, the distance between cold spot and reaction point will be

$$D = \frac{R_{Hg}}{5.5 \times 10^{-3}} = P_{Hg} \times 7.4 \times 10^3 \text{ inches}$$

The table blow gives D as a function of cold spot temperature.

Temp. of Cold Spot ($^{\circ}$C)	D (inches)
20	8.9
10	3.7
0	1.4
-10	0.45
-20	0.14
-30	0.036

By comparing the change in D with the 31.4 inches normally between Pirani gage and reaction point, the effect of cold spot temperature changes can be evaluated. For example, the change in Pirani gage reading caused by changing the cold spot temperature from -10°C to -20°C will be about one per cent. The higher the temperature the more critical it becomes. In practice, the cold spot is maintained at about -20°C. Dry ice slush is used as a cooling agent.

Figure II.4-8 shows the experimentally determined effect of changing the cold spot temperature. Figure II.4-9 shows the effect of changing the temperature of the mercury pool.

f. Relation of ionized gas to sample gas

The ionization occurs in the ionization chamber. The composition of the gas in this chamber is determined by that of the residual gases plus that which flows in via the gas inlet system. The residual gas pressures are, under operating conditions, negligibly small in comparison to the gas pressure developed by the inflowing gas. Only in the case of very small percentages of impurity is the residual of importance. Accuracy for small per cents of impurities may in some cases be improved by subtracting residual.

A much more difficult problem arises in the reduction of the plant gas pressure to a pressure sufficiently low for the proper operation of the line recorder. The pressure reduction is accomplished with an adjustable leak, merely an adjustable constriction of very small dimensions. At the low pressure end the flow is that of gases at low densities. As mentioned in Section I-2 the resistance to flow at low pressures varies as the square root of the molecular weight. From this consideration, one might expect, with a mixture of two gases of molecular weight M_1 and N_2, the following relation to hold:

$$\frac{P_1/Q_1}{P_2/Q_2} = \sqrt{\frac{M_2}{M_1}}$$

where P_1 and P_2 are the partial pressures of the two gases at the high pressure side of the leak. Q_1 and Q_2 are the respective flows of the gases through the leak.

Actually, most feasible leak constructions lead to a ratio that is somewhere between one and $\sqrt{\frac{M_2}{M_1}}$. Furthermore, the ratio depends upon the pressure on the high pressure side. If it were possible to use as a leak a small hole in a thin diaphragm, the factor would probably be $\sqrt{\frac{M_2}{M_1}}$ and would very likely be independent of pressure. The solution, however, was obtained by making the ratio unity. This was accomplished by inserting a capillary 5 inches long and 6 mils inside diameter between the adjustable leak and the system to be sampled. This does not prevent the leak from fractionating or separating but compensates for it by permitting the formation of a region just prior to the leak wherein the composition of the inflowing gas is changed and in such a way that the resulting ratio of flow through leak to partial pressure in sample is the same for all components.

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Consider the case of 616 and air. The air flows through the leak faster than the 616. This depletes the air concentration prior to the leak. To compensate for this depletion, air diffuses into the region. The rate of diffusion, however, is slow compared to the rate of gas flow through the capillary due to the small cross section of the capillary. A plot of air concentration prior to the leak might look approximately as shown in Figure II.4-10.

If the capillary is sufficiently long, the depletion at the point of entry from the sample lines will be insignificant. This means that the components of gas entering will be in constant proportion to their partial pressures. By the conservation of mass it may be concluded the gas components coming out the low pressure side of the leak are also in constant proportion to their partial pressures in the sample lines. By selecting a capillary of proper dimensions this constant proportionality may be maintained over the range of flows and pressures likely to be encountered in plant operation. Figure II.4-11 gives the experimentally determined relation between sample analysis and pressure in sample lines. The curve was obtained with a standard leak and capillary by varying the sample pressure while keeping the Pirani gage constant through readjustment of the leak. On Figure II.4-12 are shown curves taken in the same way for similar leaks without the capillary. Note the large change in analysis with sample pressure as compared to little or no change when the capillary is used.

The capillary has an undesirable action in that it increases the time required for a change of composition in the sample lines to register on the line recorder output. The added time is that required to displace the volume of the capillary at the flow rate used. For a constant flow rate, the time will obviously increase in proportion to sample line pressure. While it is difficult to measure the time lag due to the capillary, the overall time response of the line recorder has been measured. Figure II.4-13 gives the results of these tests. The 616 was circulated through the sample lines at a definite pressure, a small quantity of air then introduced, and the line recorder air peak measured as a function of time. The initial delay before the peak begins to rise is due to the time required for cleaning the volume in the capillary. The time required to build up to full value after the peak begins to rise is due to the time constant of the gas inlet lines.

g. Relation of Ions formed to Gas Composition

The production of ions by electron bombardment has been discussed in Section I-4. The number of ions formed depends upon the energy of the electrons, the number of electrons, the gas pressure, and the type of gas. Theoretically, the dependence on the number of electrons and on gas pressure is that of straight proportionality at least in the range of pressures and electron currents likely to be

encountered in line recorders. Figure II.4-14 shows the experimentally
determined relation between emission and ion currents, for various gases.
The ion currents in this case are measures of the number of ions formed.
The relation between Pirani gage and 14 peak shown in Figure II.4-5 is
essentially that of pressure versus number of ions since the Pirani gage
reading is proportional to flow which in turn is proportional to pressure.
In Figure II.4-15 the experimentally determined relation between ion cur-
rents and electron energy is shown for various gases. The data were ob-
tained by using a mixture of gases rather than running each gas individ-
ually. These curves are similar to the ionization efficiency curves dis-
cussed in Section I-4. They differ in that the variation in ion current
with electron energy is due not only to changes in ionization efficiency
but also other effects such as changes in electron distribution and sub-
sequent changes in relationship between measured ion current and number
of ions formed.

      It is evident that emission current and electron energy must
be carefully controlled if consistent results are to be obtained. Elec-
tronic regulators are used to maintain both emission and electron energy
constant. In some cases where ions of two or more different masses are
formed from the same gas it is possible to choose a particular kind of
ion which displays less tendency to change with electron energy. As an
example, take the case of 816, which produces ions of various masses
such as those which give the 69, 31 and 131 peaks shown in Figure II.4-15.
For large amounts of 816 the 69 peak is too large to be measured. This
necessitates the reading of one of the other smaller peaks such as the
31 or 131. From Figure II.4-15 it is evident that from a standpoint of
fluctuations in electron energy the 131 peak would yield the more con-
sistent results.

      It was stated that the number of ions formed is directly pro-
portional to pressure and Figure II.4-5 was offered as experimental evidence
of this fact. This assumes constant resistance to flow at the ioniza-
tion chamber since the pressure in the ionization chamber is determined
by the product of flow and resistance to flow. Any variation in resist-
ance to flow at the ionization chamber will change the number of ions
formed for a given flow and hence give inaccurate analyses. The resist-
ance to flow is determined by the geometry of the line recorder tube,
pumping lead, and the effective resistance of the mercury diffusion
pump and cold trap. The geometry is constant but the effective re-
sistances vary to some extent with the temperature of the cold trap
and the temperature of the cooling water for the diffusion pump. Un-
like the previous case concerning the resistance to flow at the Pirani
gage, these effective resistances constitute approximately 10 per cent
of the resistance to flow at the ionization chamber. In Figure II.4-16
is shown the measured change in ion current with change in average tem-
perature of the cooling water. The variation, in peak height with tem-
perature, is not extremely rapid and consequently a few degrees change
will be tolerable. However, the flow of cooling water should be watched
because if it is reduced appreciably a large change in temperature might

occur. Note that the 69 peak does not vary in the same manner as the other peaks. This is due to the fact that it comes from 816 which is condensed in the cold trap and consequently is not affected by a change in the mercury diffusion pump.

Once one has established a consistent method of forming ions, an adequate system of forming ion currents which may be measured on the feedback amplifier must still be provided. This is the function of the source and magnetic analyzer. Briefly, the ions formed in the ionization chamber are subjected to a series of electric fields which collimate the ions into a beam and impart to each ion a definite amount of kinetic energy. The beam is then passed through a magnetic field which separates the beam into a series of converging beams containing ions of a particular type. The individual beams diverge one from the other. Each of the beams are in turn brought to focus on an exit slit which allows it alone to pass through and hit the collector. The focusing of a particular beam on the exit slit is accomplished by adjusting the total voltage used to accelerate the ions at the source. By changing the total accelerating voltage different ions are brought to focus on the exit slit. Because of the wide range of mass involved the ion source must be made to function over a wide range of voltage. Difficulty arises in that there is a tendency for ion sources to become less efficient at low voltages. The ion source used in the line recorder is designed to maintain satisfactory efficiency over the range of voltages involved. The actual change in efficiency has been measured for the line recorder source and is shown in Figure II.4-17. Stabilized voltage supplies maintain constant efficiency at a given voltage. In addition to the requirement of consistent efficiency, the ion source must be capable of forming a sufficiently compact beam of ions. If the beam is too thick the analyzer will be unable to adequately separate the ions of different mass. The separation of mass 28 from mass 29 at the collector end of the line recorder is about 2.7 millimeters. Since the collector slit is 1.6 millimeters wide, an ion beam over 1.1 mm. thick would mean that in scanning the spectrum between the 28 and 29 peaks no point could be found where no ions were hitting the collector. This does not mean that 28 and 29 peaks are not resolved. Total separation of 28 and 29 is obtained until the thickness of the ion beam exceeds 2.7 millimeters. The ion source employs a series of plates which, when held at the proper voltages, enable the formation of electric fields which collimate and focus the ions into a beam sufficiently thin. A pair of split plates is provided to enable compensation for any mechanical misalignment or displacement of ions due to the magnetic field of the source magnet.

In the experimental determination of source characteristics, a system similar to that used for multi-element radio tubes is employed. The potential of J5 was chosen as the independent variable and curves determined for various combinations of voltages on J1 and J3. In every case the voltage on J2 was adjusted for maximum sensitivity; this setting

for the most part remained constant with a given voltage on J1. Tests
were conducted on four line recorders and as with radio tubes the char-
acteristic curves obtained were found to be similar in shape but not
exactly alike. A typical set of characteristic curves are shown in
Figures II.4-18 to II.4-25. (For these machines the emission regulator
was so constructed that the fine adjustment was on J2, not J1).
Not plotted on the graphs is the ratio of 28 to 29 peak. This ratio
was found to remain constant even though the 28.5 to 29 ratio became
unity, indicating the 28 and 29 peaks are resolved even with the poor
"apparent resolution".

h. Overall Performance of the Line Recorder

Tests indicate that the line recorder design is satisfactory
and practical. One unit has been in continuous operation for six months,
during which time it has been used to run analyses for a pilot plant.
The entire set up including the manifolding were similar to that which
is to be used in the plant, although on a smaller scale. The pilot
plant analyses obtained from these operations were found to be accurate
and reliable. Theoretical considerations as well as other methods of
measurement permitted a close check on their accuracy. In view of all
tests made it is believed that measurements accurate to within two
per cent of the measured value can readily be attained. Careful oper-
ation can undoubtedly improve upon this figure. The two per cent accu-
racy, of course, does not necessarily apply to measurements involving
very small or very large amounts of impurity. Figure II.4-1 gives
the overall performance as determined by the analysis of calibration
samples. Samples were prepared from day to day and any inaccuracies
in sample preparation would appear on Figure II.4-1. The smallest
amount of impurity which may be measured with a given accuracy de-
pends upon the gas. In general the readings become inaccurate when
the impurity peak is but a few times greater than the residual peak
at the same mass. For air and fluorocarbons measurements of very
low percentages are possible while gases such as HF and BF_3 cannot
be measured with accuracy even though they constitute a per cent or
more of impurity.

When a machine is first put into operation some time is re-
quired before accurate analysis can be made. Tests on several mach-
ines showed that 10 hours or so would be ample even under the most
unfavorable conditions and in most cases far less time would be re-
quired. The results of tests on one machine is shown in Figures
II.4-26 and II.4-27. Moist air was allowed to stand in the entire
tube and manifold for twelve hours before starting the experiment.
Zero time coincides with the point at which the pumps were started.

i. Typical Operating Conditions

It is intended to summarize here the manner in which the
various components of a line recorder and the line recorder as a whole
may be expected to operate when all goes well. These data have been ob-

tained from a study of five line recorders operating simultaneously over a period of a few months. These data may be used as a guide in judging whether any line recorder, when recently started up, is performing properly.

When the line recorder is prepared for operation in the manner presented in Section II-2 one may expect to find that the items listed in the following table hold fairly well.

Potential between shield and J1	100 volts
Potential between shield and J2	105 volts
Potential between shield and J3	120 volts
Potential between J5 and ground	0.6 of potential between shield & ground
Potential between shield and trap	90 volts
Potential between filament & shield	75 volts
Total emission	100 microamperes
Trap current	100 microamperes
Ratio of 28 to 29 for nitrogen	120
Ratio of valley between 28 and 29 peaks to 29 peak for nitrogen	0.3
Source magnet strength at center of gap	250 gauss
Main magnet strength	3250 gauss
Mass 28 accelerating voltage	1050 volts
Source and main magnet fields in same direction	

The following data on typical residuals and sensitivities will hold for either of the following modes of operation.

grid resistor of 5×10^9 ohms and emission of 100 microamperes
grid resistor of 2×10^{10} ohms and emission of 25 microamperes

Listed below are the maximum expected values of the residuals:

Mass	Peak Height (scale Unit)
14	3
20	1000
28	40
32	5
44	50 in beginning, reduces with time
69	5 after C-816 has been run in recorder

A typical spectrum, as obtained upon the manual divider, for residuals is included as Figure II.4-28.

If 100% air is run through the line recorder with a Pirani gage reading of 50, the mass 14 peak may be expected to run between two and four thousand. The 28 peak will be off scale and the 32 peak will run between five and ten thousand. The higher end of this range is also off scale. For samples containing 1% 816, with a Pirani reading of 50, the 69 peak will be between one thousand and fifteen hundred. Typical spectra, as obtained with the manual divider, for room air and for 816 are included on Figures II.4-29 and II.4-30.

VARIATION OF LINE RECORDER
CALIBRATION WITH TIME

TIME IN DAYS

14 PEAK
PIRANI

FIGURE II.4-1

FIGURE II.4-2

DEPENDENCE OF PIRANI GAGE READING ON AMBIENT TEMPERATURE

FIGURE II.4-3

STATIC CALIBRATION CURVE
OF PIRANI FOR NITROGEN

Percent Static Response (%)

N₂ Pressure (MICRONS)

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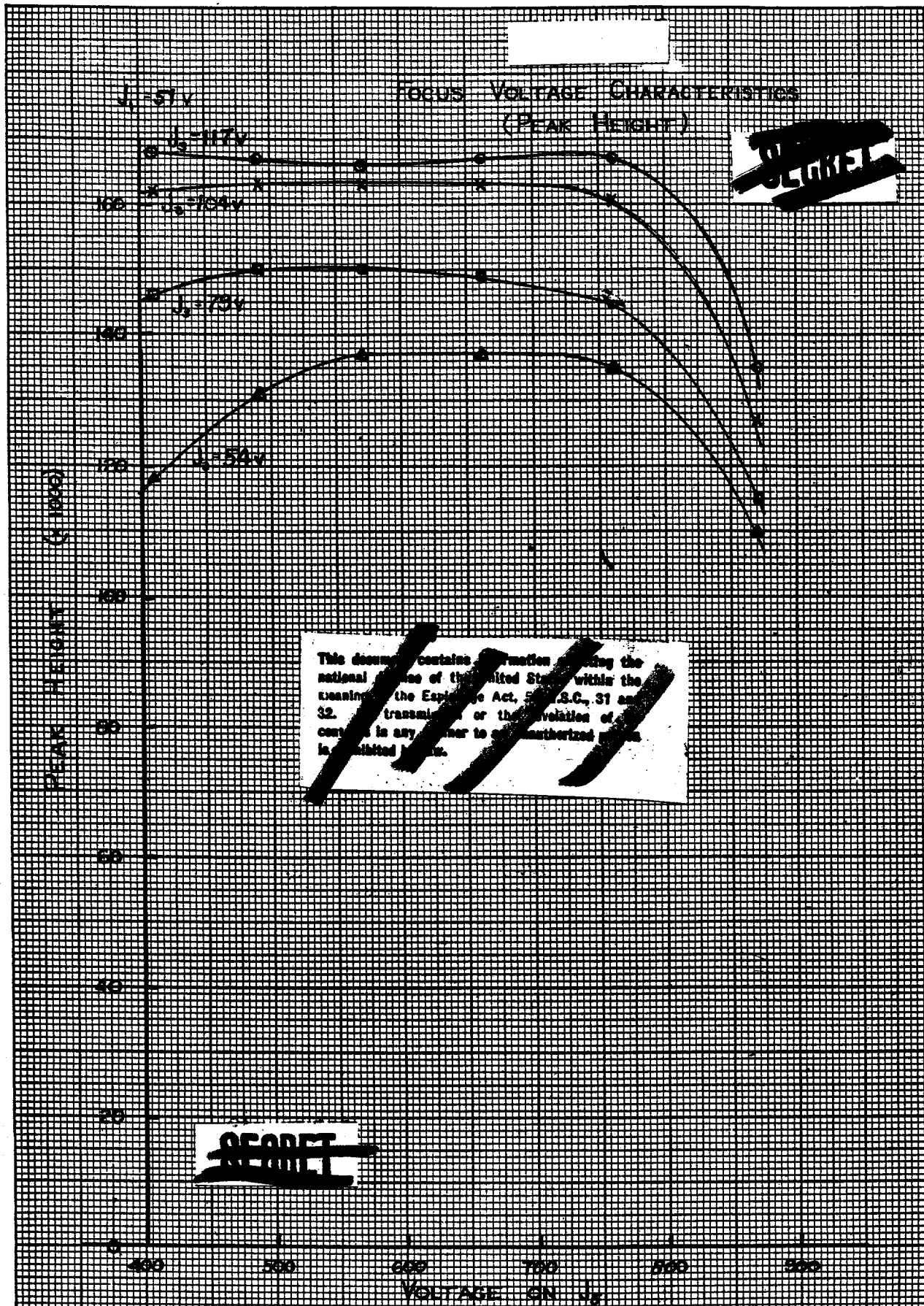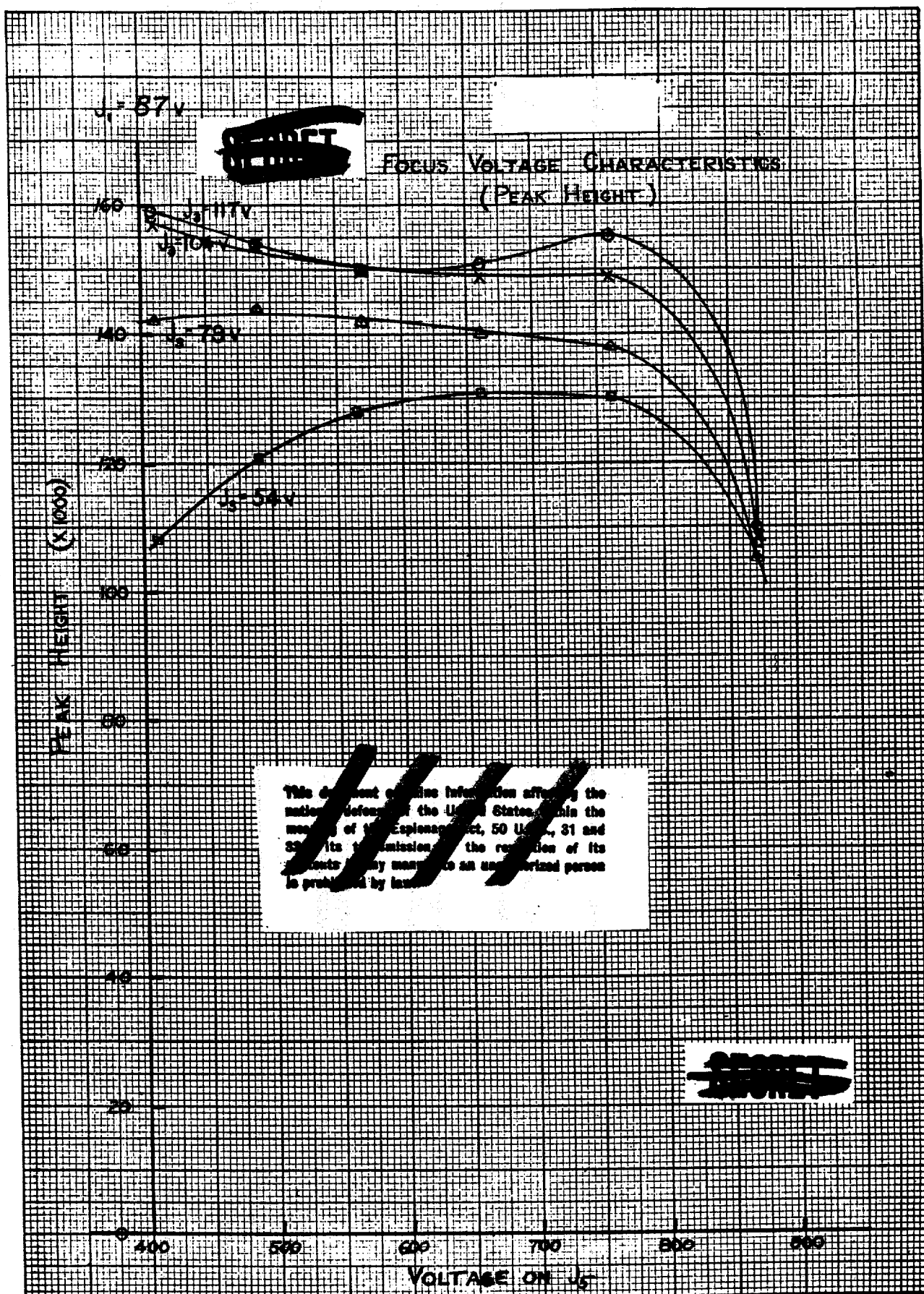is prohibited by law.
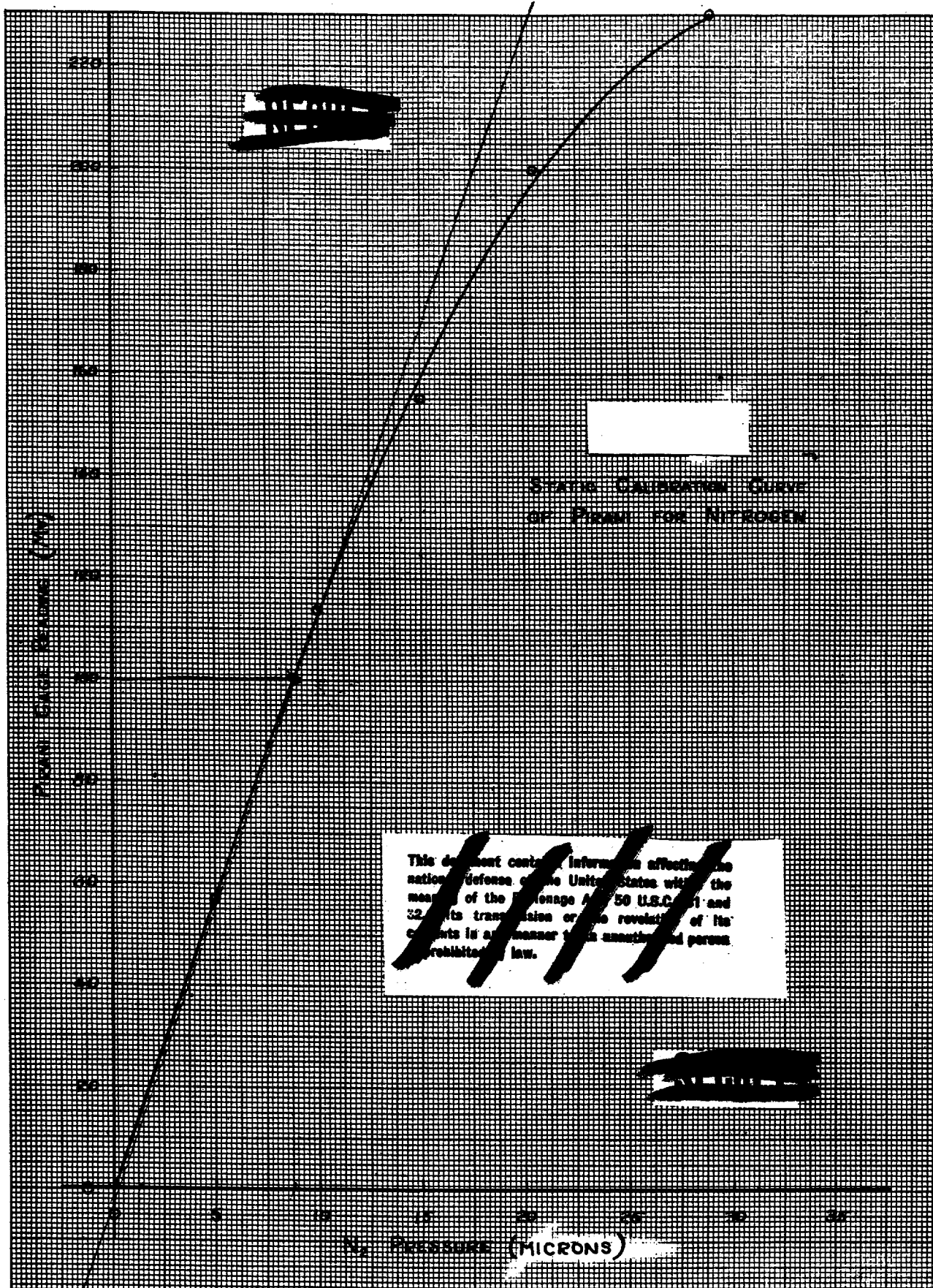
FIGURE II.4-4

PIRANI GAGE CHARACTERISTICS

MASS 14 PEAK
vs
PIRANI GAGE READING

PIRANI GAGE READING
m.v.

SAMPLE OF GAS - 10% AIR

X - Flow Rising
○ - Flow Falling

FIGURE II.4·5

GAS INLET LINES

GAS INLET LINES
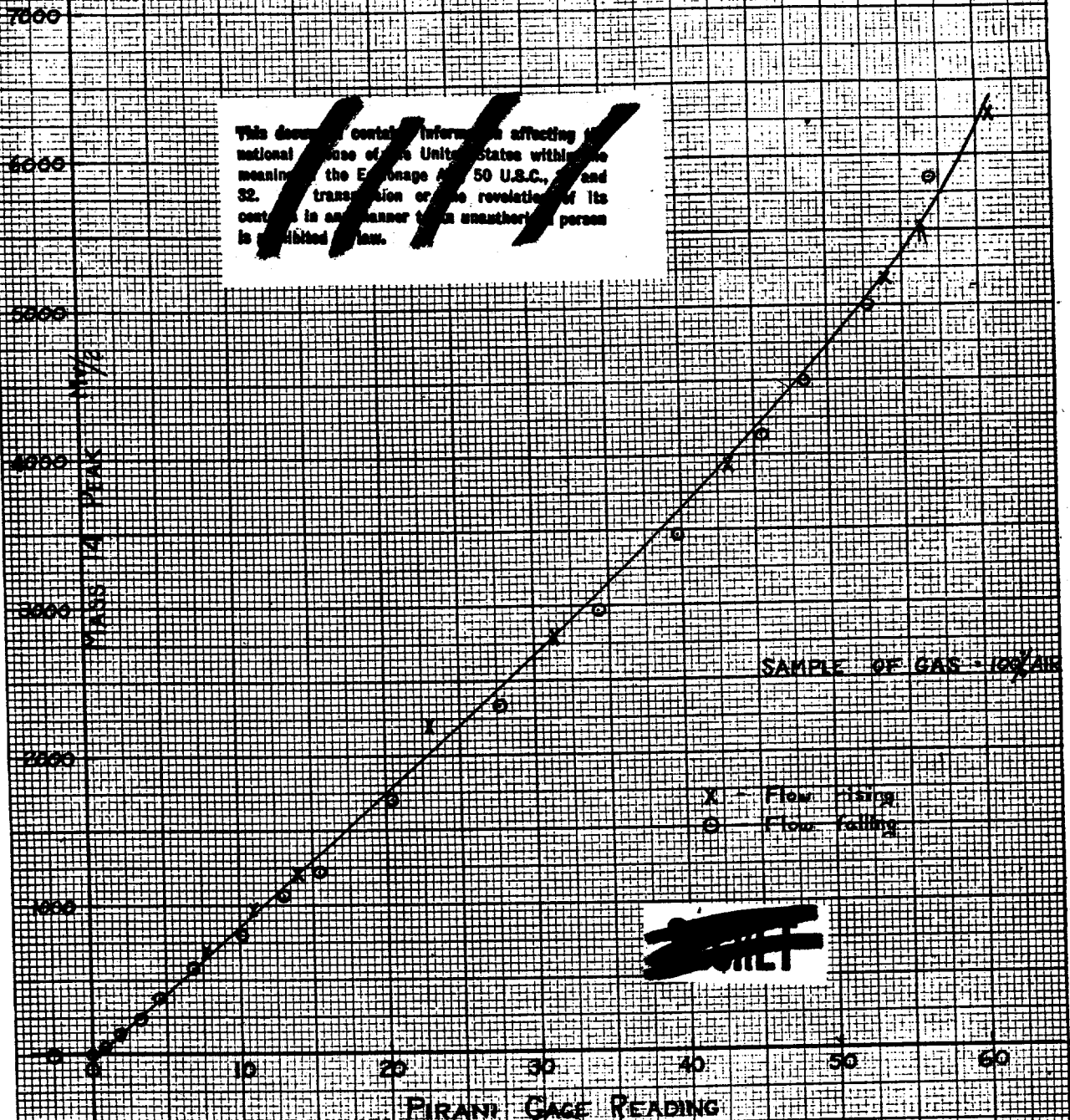
FIGURE II.4-6

FIGURE II.4-7

TITLE- CHEMICAL TRAP

THE KELLEX CORPORATION
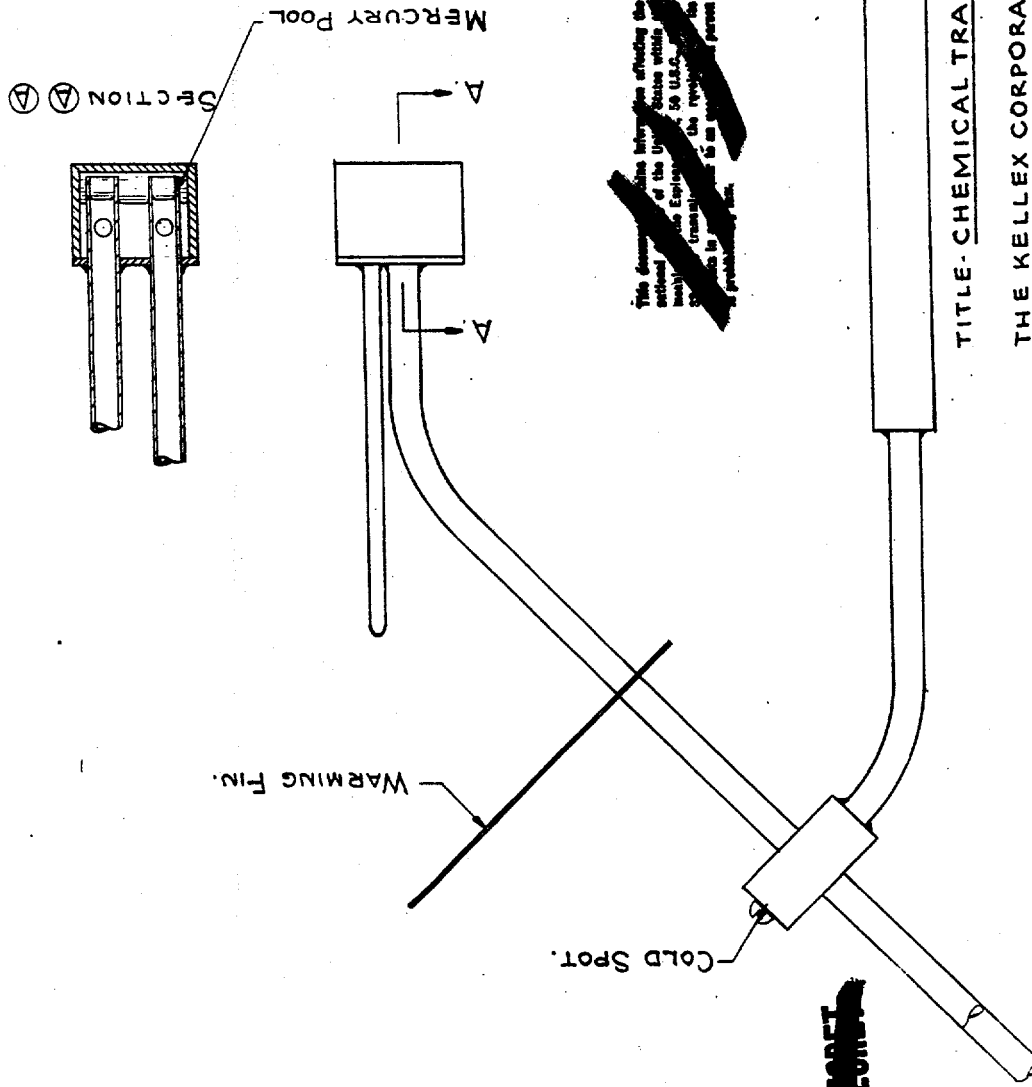
FIGURE II.4-8
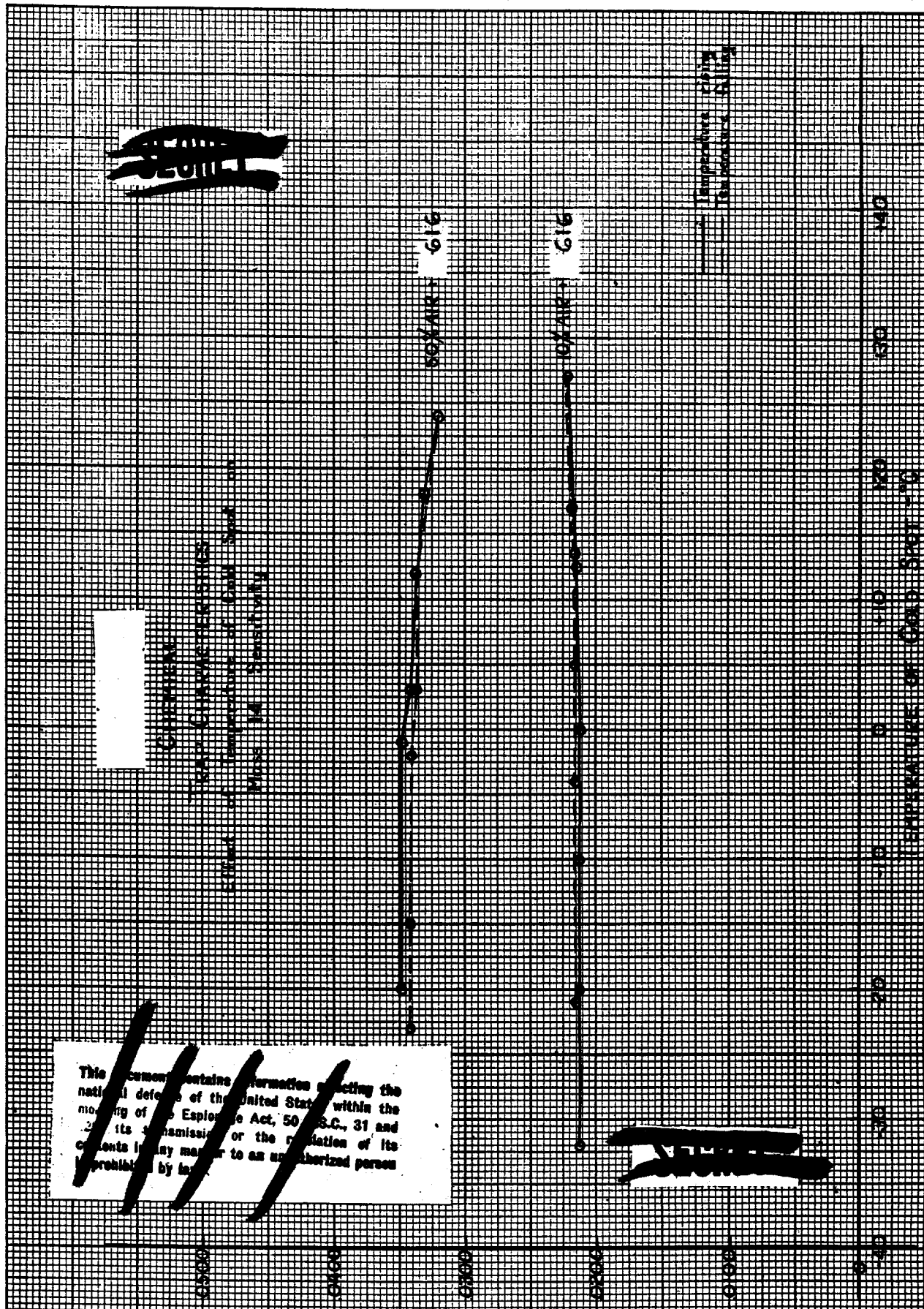
CRITICAL GAP CHARACTERISTICS

Effect of Temperature of Mercury Pool
On Mass 14 Sensitivity

IOK AIR 1618

TEMPERATURE OF MERCURY POOL °C

PIRANI × % AIR

MASS 14 PEAK

0.400
0.600
0.200
0.000

.40 .50 .60 .70

FIGURE II.4-9

VARIATION OF AIR CONTENT
OF GAS WITH POSITION IN CAPILLARY

FIGURE II.4-10

VARIATION OF MASS 28/ARGON GAGE
WITH PRESSURE BEHIND LEAK
(WITH CAPILLARY)

MASS 28/ARGON

SAMPLE — 12.0% AIR
97.5% ± 816

PRESSURE — CM OF Hg

FIGURE II.4-11

VARIATION OF MASS 28/PARAM LEAK
WITH PRESSURE BEHIND LEAK
(WITHOUT CAPILLARY)

FIGURE II.4-12

TIME RESPONSE TO SUDDEN CHANGE IN CONCENTRATION (USING B-4 PUMP)
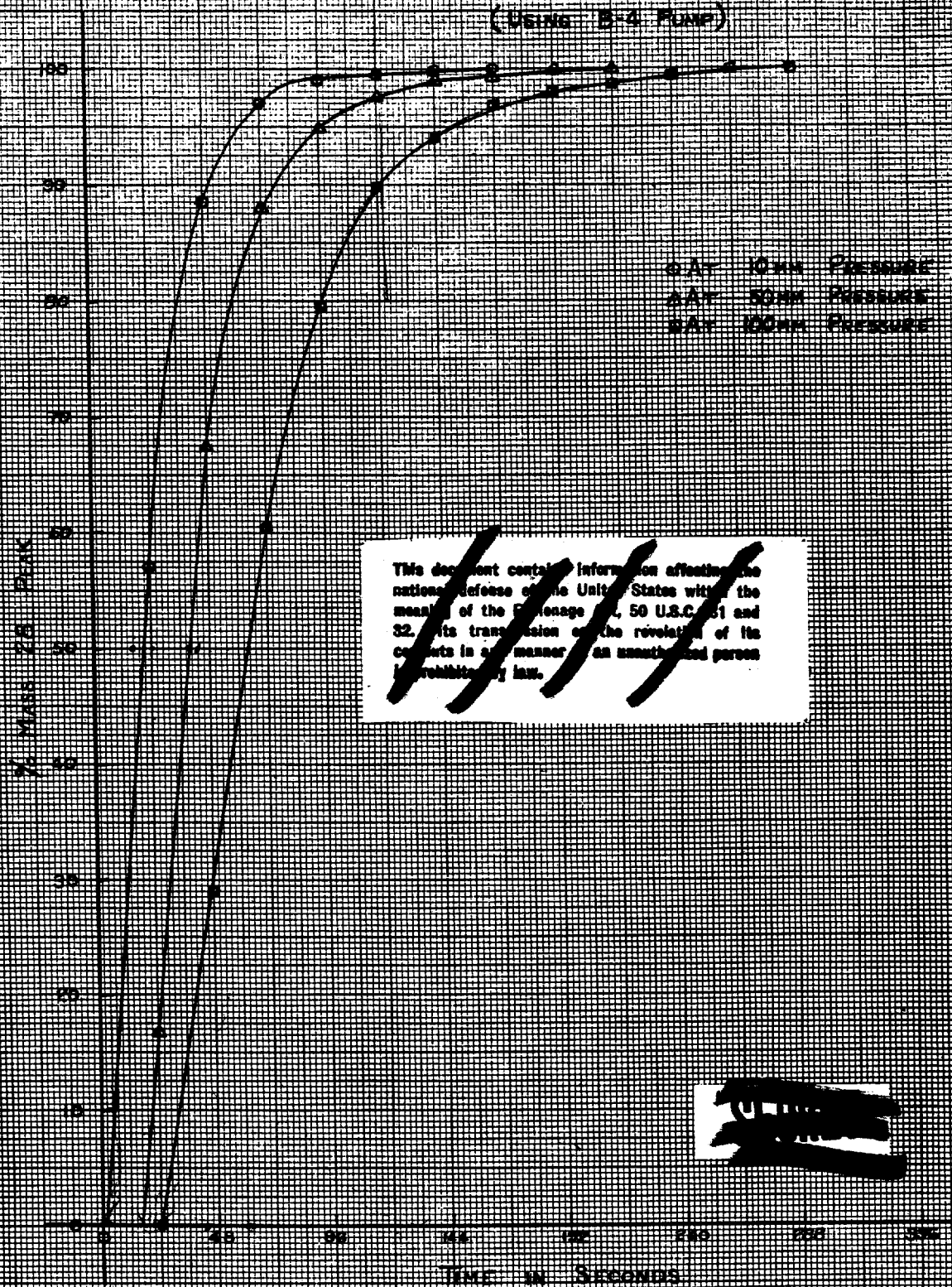
○ AT 10 MM PRESSURE
△ AT 50 MM PRESSURE
□ AT 100 MM PRESSURE

% Mass 70 Peak

TIME IN SECONDS

FIGURE II.4-13

VARIATION OF PEAK HEIGHT WITH EMISSION
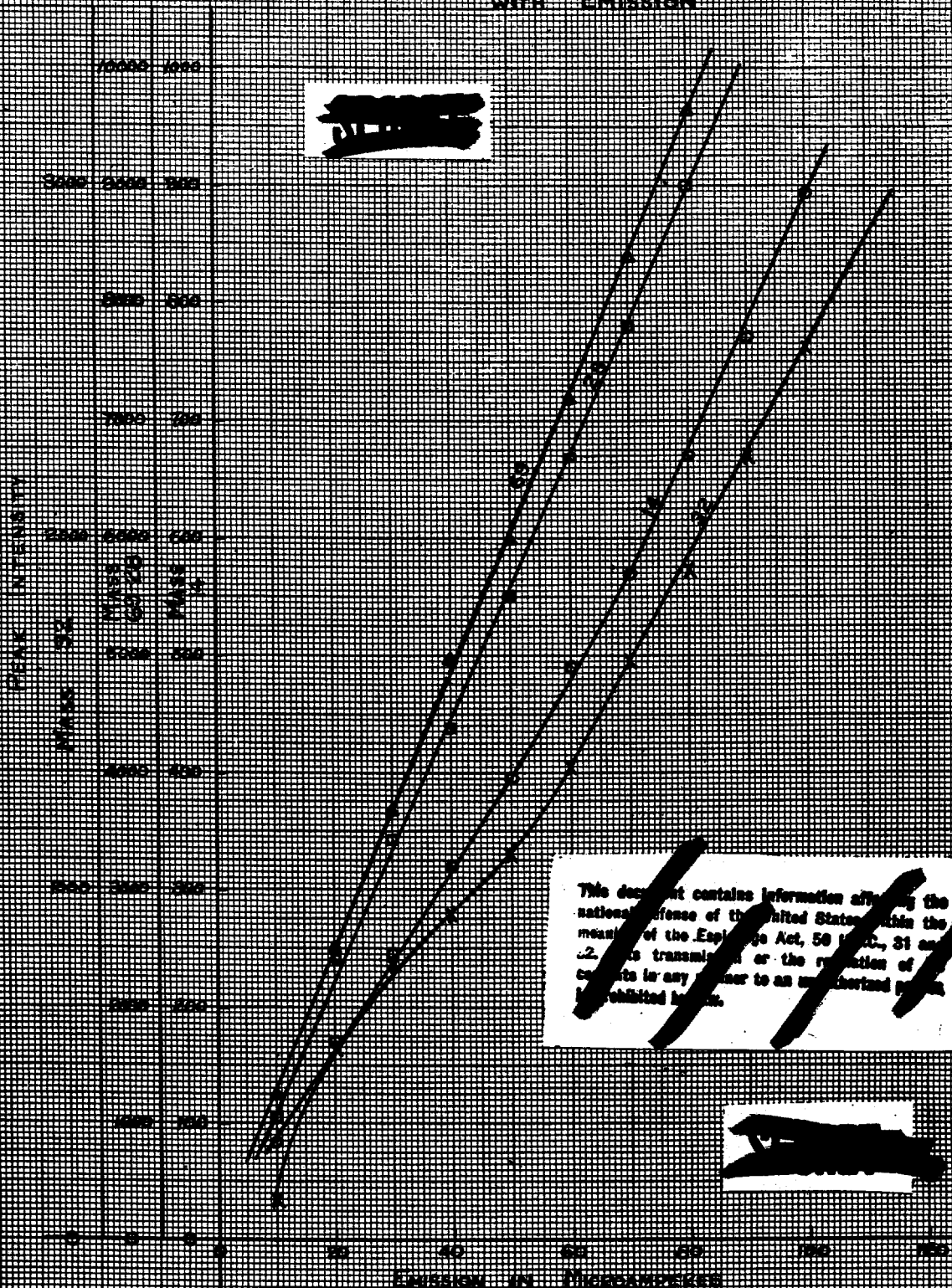
FIGURE II.4-14

VARIATION OF PEAK HEIGHT
WITH ELECTRON ENERGY

FIGURE II.4-15

EFFECT OF COOLING WATER
ON PEAK HEIGHT
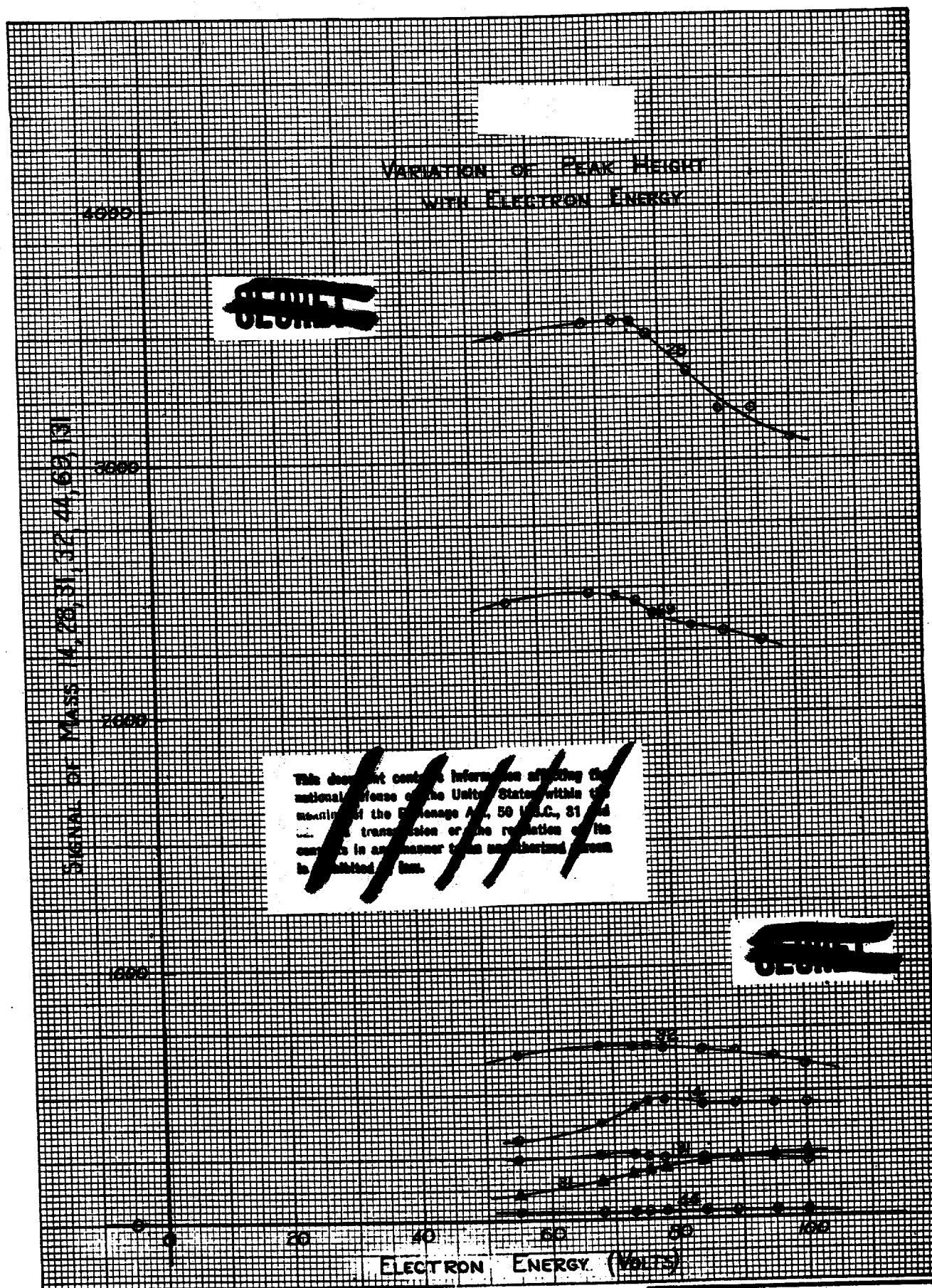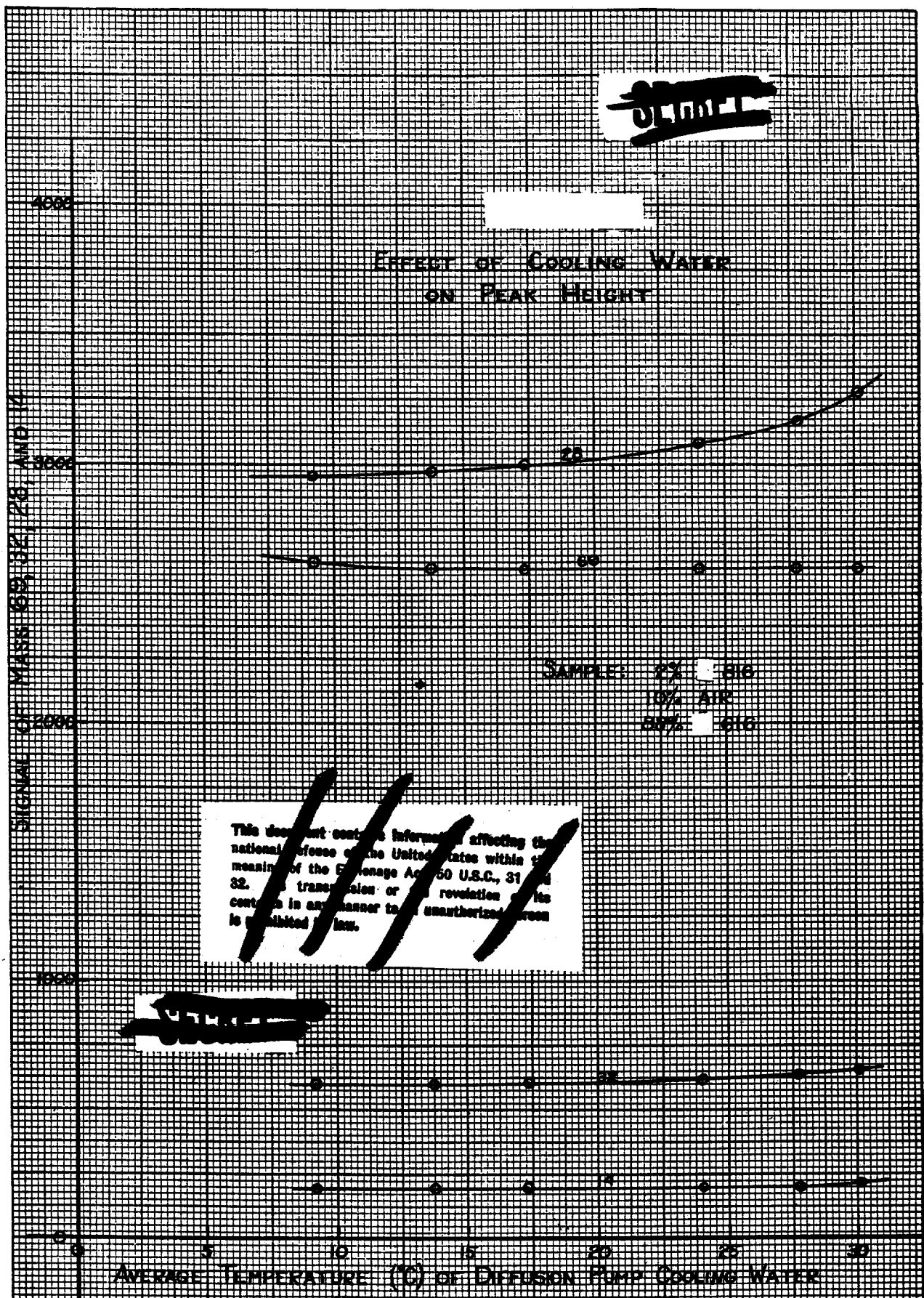
FIGURE II.4·16

VARIATION OF ION CURRENT WITH ACCELERATING VOLTAGE
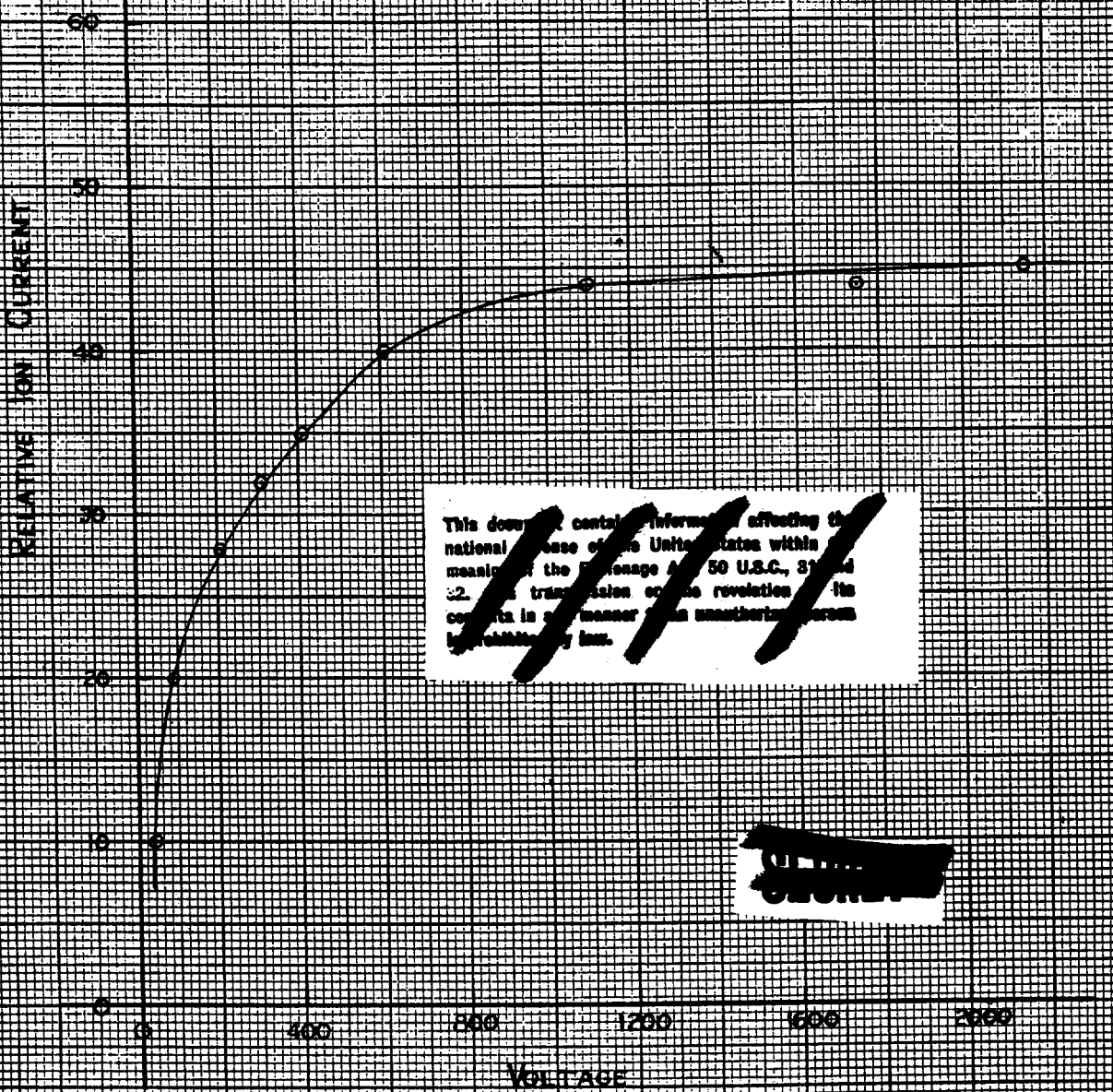
FIGURE II.4-17

FOCUS VOLTAGE CHARACTERISTICS
(APPARENT RESOLUTION)
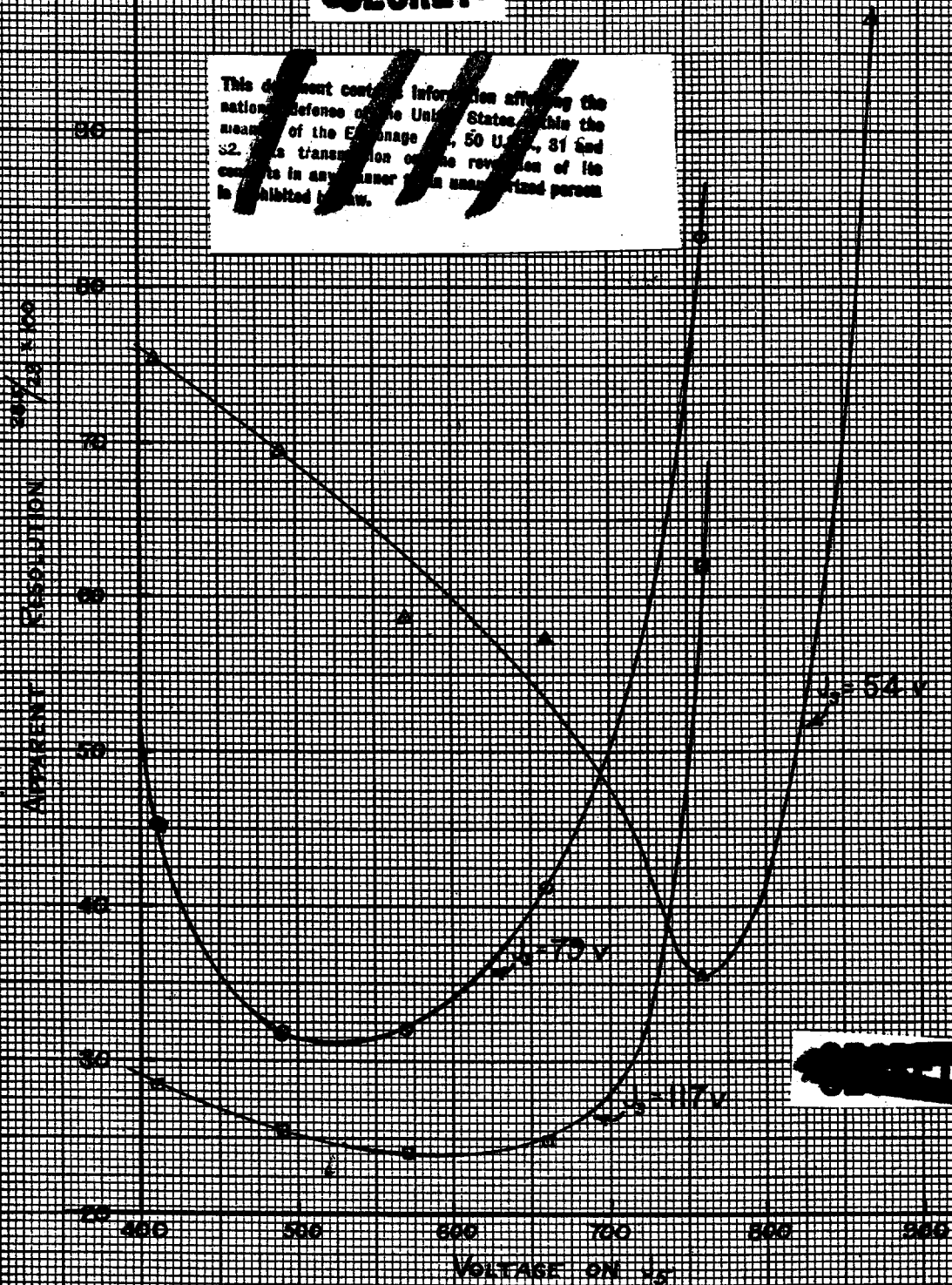
FIGURE II.4-18

FOCUS VOLTAGE CHARACTERISTICS
(APPARENT RESOLUTION)

FIGURE II.4-19

FOCUS VOLTAGE CHARACTERISTICS (APPARENT RESOLUTION)
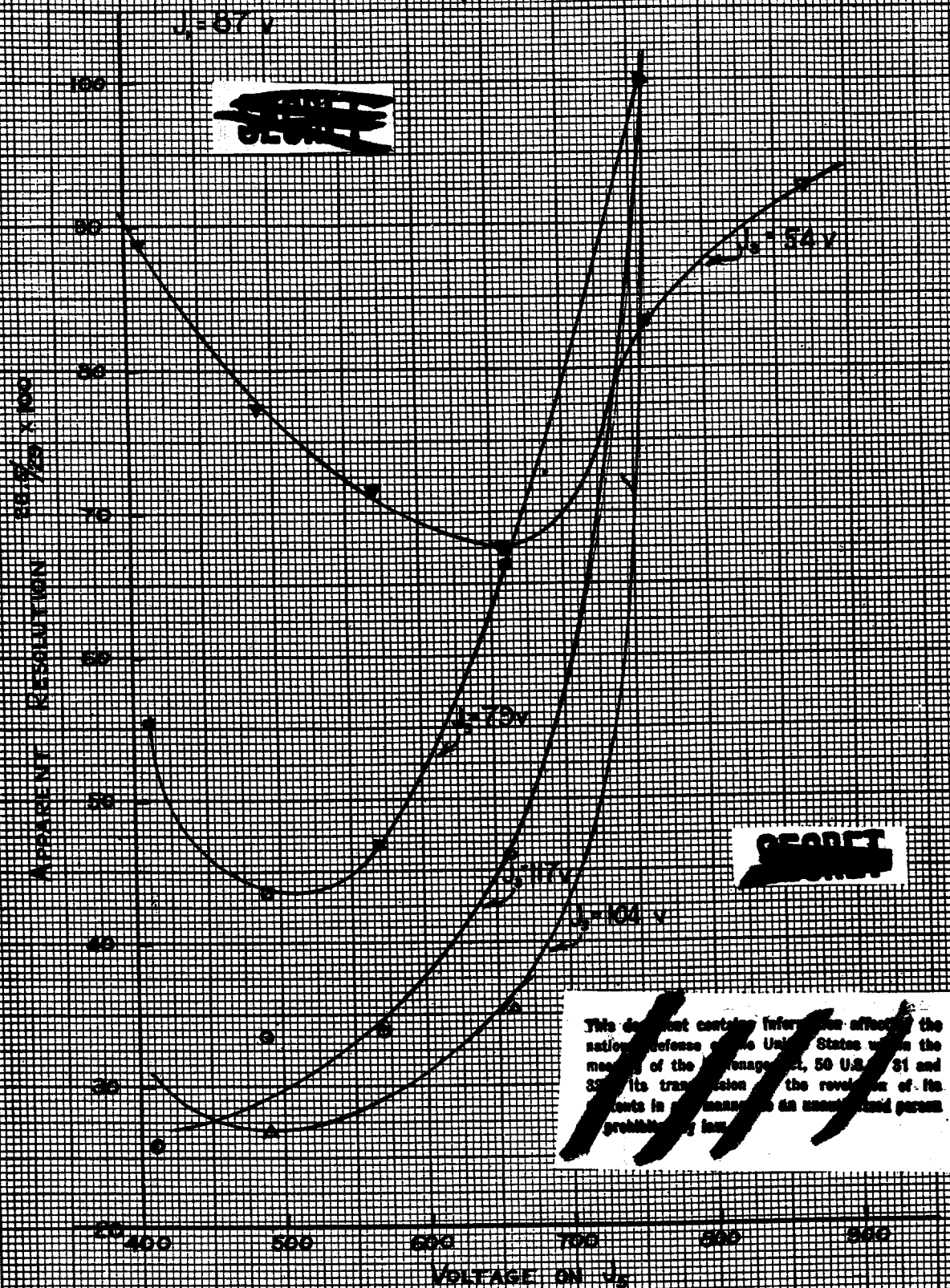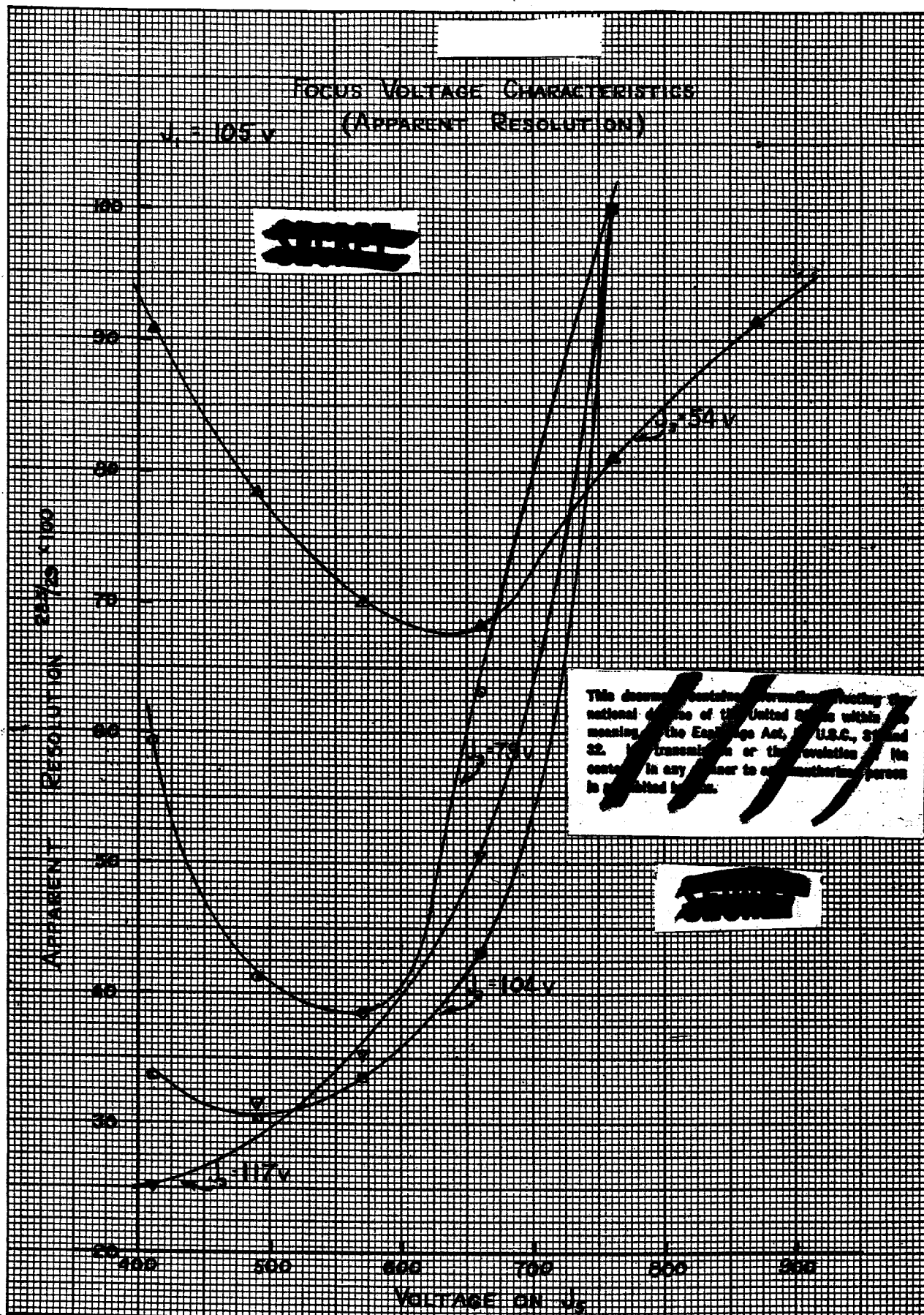
FIGURE II.4-20

FOCUS VOLTAGE CHARACTERISTICS
(APPARENT RESOLUTION)
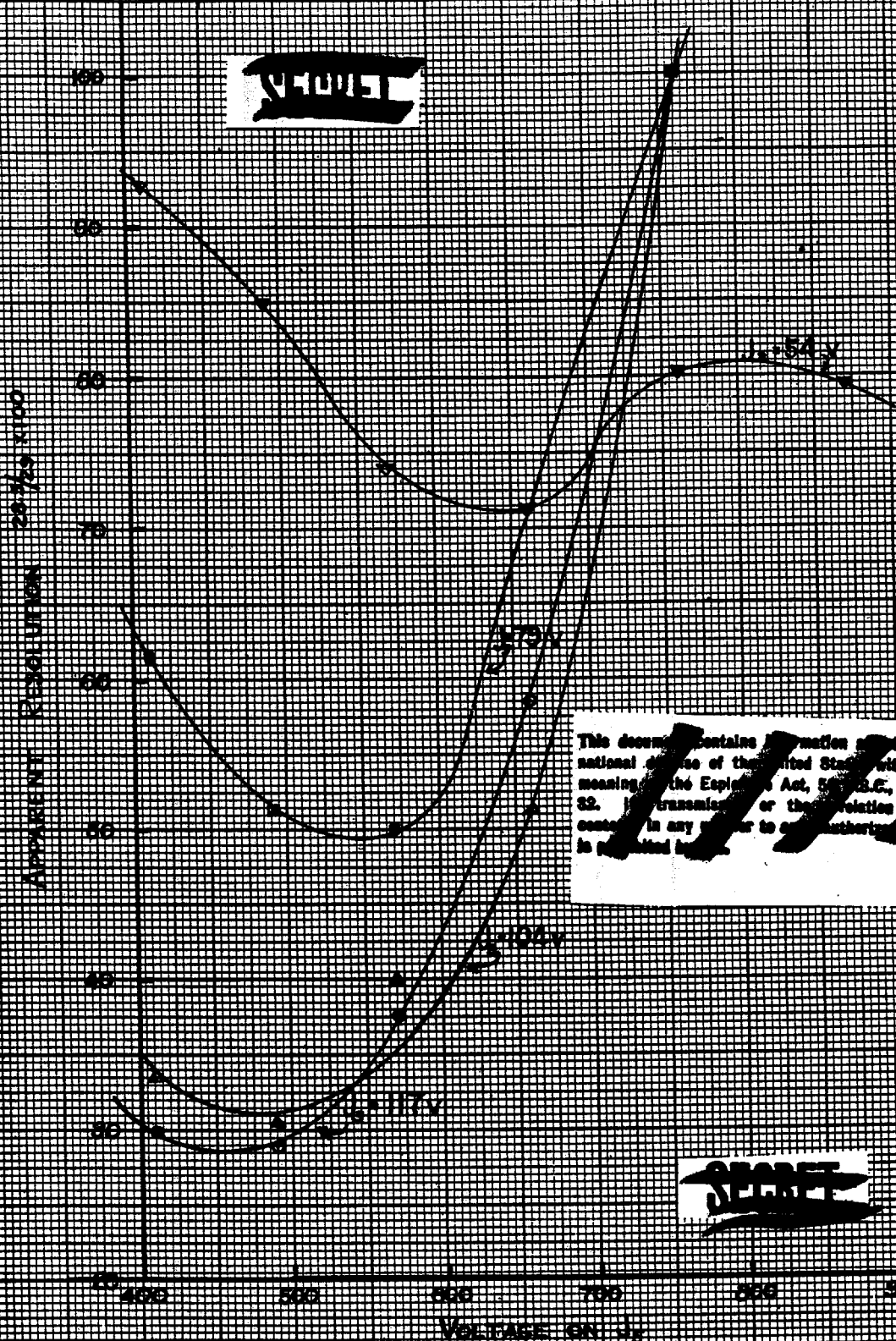
FIGURE II.4-21

FOCUS VOLTAGE CHARACTERISTICS
(PEAK HEIGHT)

FIGURE II.4-22

FIGURE II.4·23

FIGURE II.4-24

FOCUS VOLTAGE CHARACTERISTICS
(PEAK HEIGHT)

FIGURE II.4-25

FIGURE II.4-26

SAMPLE 1372 AR 3X74 616

VARIATIONS OF RESPONSE TO STIMULUS
VARIOUS
AS REQUIRED
ALSO SAMPLE

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FIGURE II.4-27

SPECTRUM OF RESIDUAL
GAS IN SPECTROMETER.

ACCELERATING VOLTAGE.

S-GNAL M.V.

FIGURE II.4.28
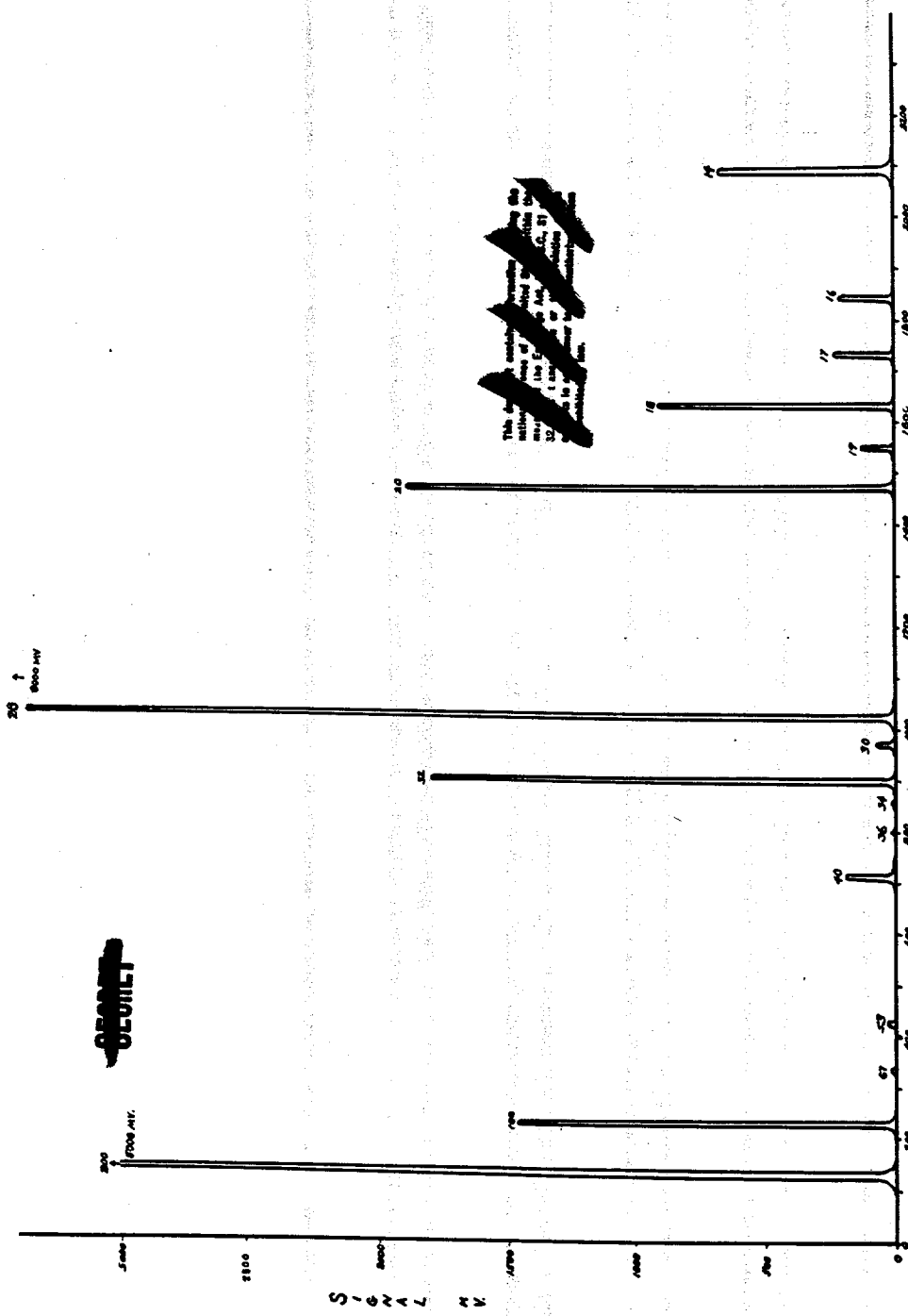
THE KELLEX CORP.

FIGURE II 4.29

TITLE Spectrum of Room Air

THE KELLEX CORP.

FIGURE II.4-30

THE KELLEX CORPORATION

CRACKING PATTERN OF 8/6

VOLTAGE
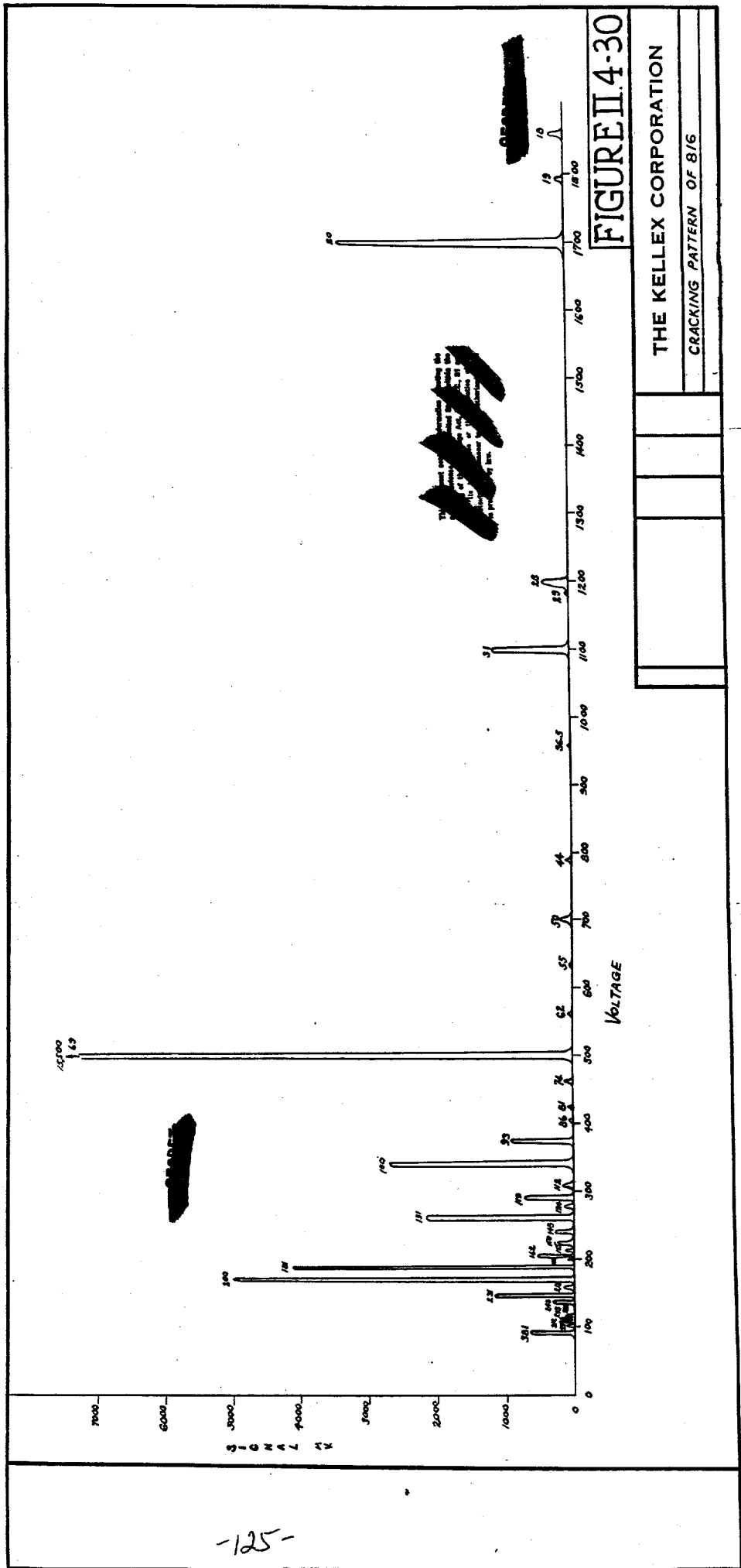
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